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Trace-Element Characterization of Coal Wastes - Fifth Annual Progress Report

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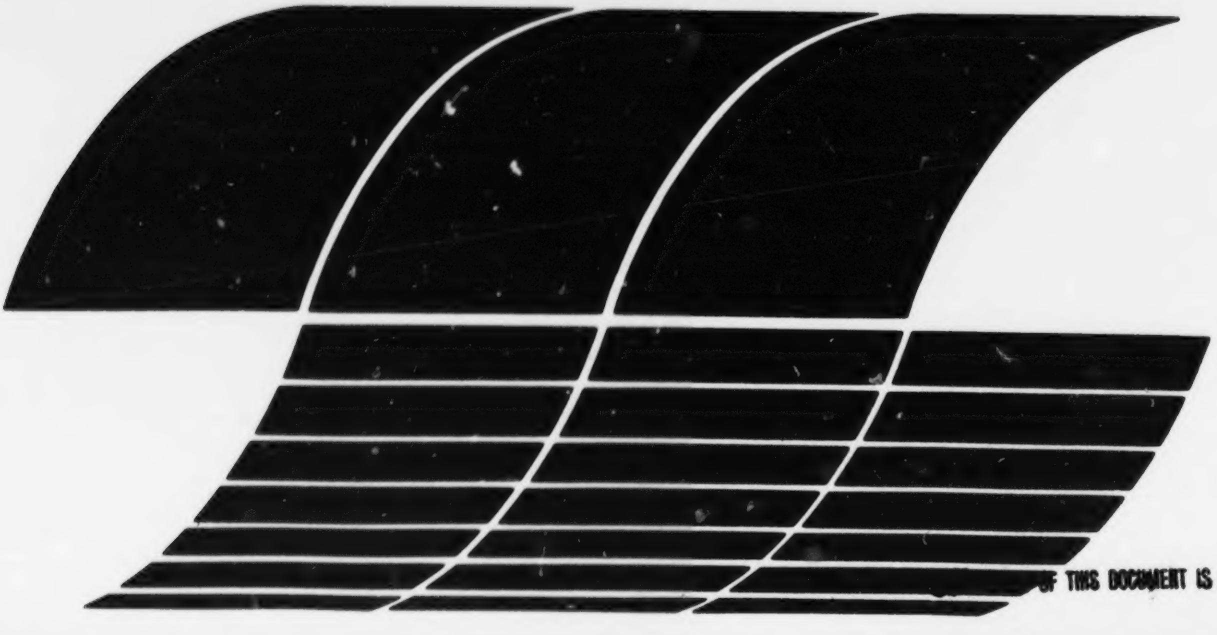

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Trace-Element Characterization of Coal Wastes -
Fifth Annual Progress Report

October 1, 1979 — September 30, 1980

by

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FIFTH ANNUAL PROGRESS REPORT
TRACE ELEMENT CHARACTERIZATION OF COAL WASTES

October 1, 1979—September 30, 1980

by

R. C. Heaton, L. E. Wangen, P. L. Wanek, J. M. Williams,
E. F. Thode, M. M. Jones, A. M. Nyitray, P. Wagner, and J. P. Bertino

ABSTRACT

During the past year we continued our research on environmental control technologies as they relate to coal preparation wastes and extended our assessments to include studies of high-sulfur Appalachian coal cleaning wastes.

The most promising control technology for dealing with high-sulfur coal wastes consists of sequential slurry coating of the waste with lime and limestone. In the configuration tested (0.35% lime and 1.1% limestone), this technique controlled the waste effluent quality for 4 months; the effluent pH remained between 7.3 and 7.6, and the trace element concentrations (Al, Ca, Mn, Fe, Co, Ni, Cu) were within acceptable limits according to the Environmental Protection Agency Multimedia Environmental Goals/Minimum Acute Toxicity Effluent system of evaluation. Codisposal of coal wastes and alkaline soils or mine overburdens is partly effective in controlling the leachate quality under steady-state conditions. However, none of the materials tested could control the highly acidic effluents obtained under intermittent leaching conditions.

Comparisons between trace element concentrations predicted by chemical equilibrium models and those obtained in experiments with coal waste leachates yielded good agreements for the major cations (Al, Ca, Fe) but, except for fluoride, the major anions were not well accounted for. The observed trace element concentrations were all significantly lower than predicted.

Calcination experiments have shown that high-sulfur coal waste from Appalachia (Plant K) behaves differently than other wastes we have studied. The high cost of this technology ($1.39 to $9.84/ton product) places it outside the realm of economic feasibility at this time.

We have also completed an assessment of the Plant K coal wastes. These materials are similar to those from the Illinois Basin and their leachates are often very acidic, with pH values sometimes less than 2. Several trace elements have shown discharge severities greater than unity (Fe, As, Ni, Mn, Al), but iron is by far the worst offender, with values sometimes greater than 100.

Results of the EPA Extraction Procedure, used to classify solid wastes under the Resource Conservation and Recovery Act, compare favorably with those of our own leaching experiments for those elements analyzed (Ag, As, Ba, Cd, Cr, Hg, Pb, Se). However, coal wastes release substantial quantities of other trace elements not included in the protocols at present (Fe, Al, Ni, Mn, Zn, Cu).

EXECUTIVE SUMMARY

In the past, our research on coal and coal wastes focused on identifying trace elements released in hazardous amounts during weathering and leaching of high-sulfur coal refuse from the Illinois Basin, and on evaluating control technologies for this problem. Present efforts are directed toward further development of these control technologies and extension of trace element assessments to the drainages from high-sulfur coals and coal wastes from Appalachia. Technical highlights and accomplishments during FY 1980 are summarized in this section and more detailed discussions are contained in the main body of this report.

The drainages from many coal waste dumps are often highly contaminated with trace or inorganic elements. However, until recently there has been little concrete information on the quantities released, the controlling chemistry involved, or the ways to control these releases. Accordingly, the principal objectives of our program are to

(1) assess the nature and magnitude of trace element releases of environmental concern.

(2) reveal experimentally the chemistry controlling trace element releases.

(3) evaluate and recommend appropriate pollution control technologies or necessary research and development programs.

The studies under way are a continuation of experimental efforts begun in 1976, which were directed toward identifying and quantifying the trace element releases from high-sulfur coal wastes from the Illinois Basin. We now have a good quantitative understanding of the environmental concerns associated with these wastes and their drainages. In FY 1979 we began in-depth experimental evaluations of various technologies for controlling them. Among the methods considered were codisposal of the coal waste with neutralizing or attenuating agents, containment of waste leachates coupled with water treatment techniques, and alteration of the waste to yield an environmentally inert material. Cost analysis showed the last of these technologies to be too costly, while the first two were only partially effective, at least in the configuration studied. In FY 1980 we have continued to evaluate and improve these technologies, emphasizing those we consider to be the most promising, namely, sequential slurry treatment of the coal waste with lime and limestone and certain codisposal techniques. We also extended our trace element assessments to include coals and coal wastes from Appalachia.

Technical accomplishments of FY 1980 fall into three general areas: (1) studies of control technologies for high-sulfur coal wastes from the Illinois Basin, (2) evaluation and assessment of coal wastes from Appalachia, and (3) continuing development of procedures and techniques.

I. ENVIRONMENTAL CONTROL TECHNOLOGIES

Studies performed over the past several years show that the drainages from uncontrolled piles of high-sulfur coal wastes typically are very acidic (pH values less than 2 have been observed) and contain environmentally significant concentrations of several trace elements.[1-4] This contamination is caused by sulfuric acid generated within the waste by oxidation of pyrite. In order to eliminate the contamination one must either prevent the formation of the acid within the waste, neutralize the acid *in situ* after it is formed, or allow the leaching to take place and treat the effluents to remove the acid and trace element contaminants. Each of these approaches has advantages and disadvantages.

In situ neutralization of acid formed within a waste pile can be accomplished by mixing the coal refuse with alkaline materials either before or during disposal. We have demonstrated that if the pH of the waste effluents is maintained in the proper range, the trace element concentrations also stay within acceptable limits. The initial pH of the waste effluent can be easily controlled by adding hydrated lime to the waste, but this treatment is only temporary because any excess lime is quickly washed out of the solid refuse. Ground limestone is more durable, since it is not soluble in neutral solutions, but it cannot control the high initial acidities of high-sulfur coal waste. Although neither the lime treatment nor the limestone treatment alone is an adequate control technology, a combination of the two, using a small amount of lime to control the initial acidity and a larger amount of limestone to control the slowly generated acid within the pile, promises the advantages of both without the limitations of either. Experiments completed during FY 1980 show that this approach is very effective in controlling coal waste effluents for periods of up to 4 months.

Leachates from high-sulfur coal wastes obtained from the Illinois Basin (Plant B) typically have pH values of approximately 2.0 or less when subjected to long-term laboratory weathering experiments. However, when the same wastes were sequentially treated with 0.35% lime and 1.0% limestone and subjected to artificial weathering conditions equivalent to intermittent rains totaling 39 in. per year, the waste effluents had pH values between 7.3 and 7.6 for nearly 4 months. In addition the trace element releases were all within acceptable limits according to the EPA MEG/MATE (Environmental Protection Agency Multimedia Environmental Goals/Minimum Acute Toxicity Effluent) system of evaluation.[5] Figure 1 shows the effectiveness of this treatment in controlling trace element releases from this waste. Cost analyses carried out in 1978 show that sequential lime/limestone slurry treatment would cost between 22 and 50¢ per ton of cleaned coal (1978 dollars), which is competitive with the technologies already in use.

Although the lime/limestone slurry treatment has provided some very encouraging results, it lasts for only about 4 months under the conditions of the laboratory weathering tests. In fact, because the amount of limestone added is chemically equivalent to only about 10% of the pyrite in the waste, this treatment cannot be permanent unless oxidation of the waste is somehow prevented. However, we believe this treatment of the waste, followed by disposal in an anaerobic environment, would be useful as a comprehensive waste disposal strategy. The lime/limestone treatment would neutralize the acid initially present in the waste and control the trace element releases until the permanent anaerobic disposal could be implemented.

Some uncertainties remain concerning the lime/limestone treatment. Because this treatment has been evaluated with only one coal waste, we must determine whether the observed performance is a general phenomenon or whether it is unique to the material we tested. In addition, no attempt was made to optimize the treatment parameters. The effects of compaction of the waste pile or freeze-thaw cycles have not been studied. Finally, the mechanism by which this process works is only partially understood. All of these questions warrant study and will be addressed in the coming year.

Another way to effect *in situ* acid neutralization in coal wastes is to mix the refuse with alkaline soils or mine overburdens either before or during deposition in the waste dump. Alkaline process wastes, such as fly ash, could also be used. This possibility is attractive because it would be easy to implement and the required materials

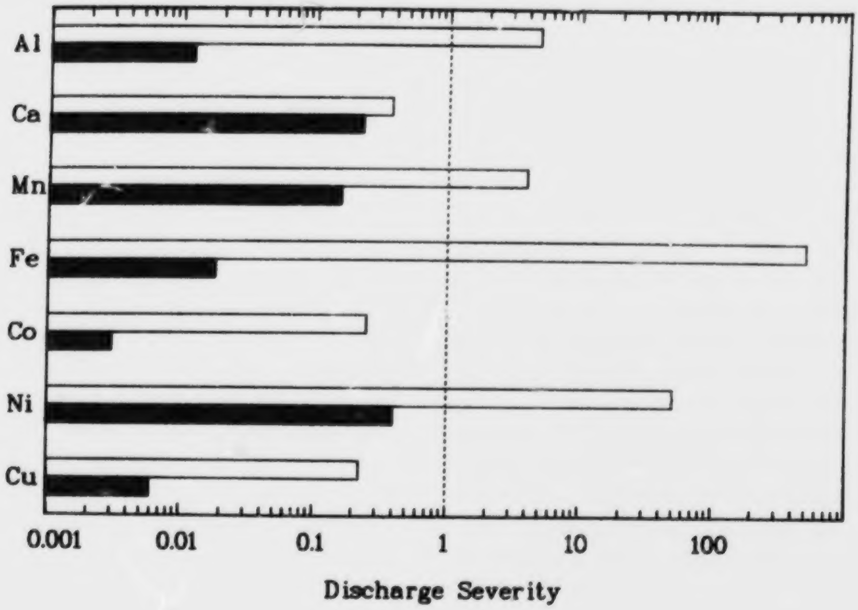

Fig. 1.
Discharge severities (leachate concentration/100 × MATE) for selected trace elements in drainages from high-sulfur coal preparation wastes—untreated wastes (unshaded) and lime/limestone treated wastes (shaded).

are inexpensive and readily available. Laboratory studies conducted this year with a variety of soils and process wastes show that alkaline materials are partly effective in controlling effluent quality when mixed in with the coal waste or placed downstream of the waste. Concentrations of aluminum, nickel, fluorine, and arsenic (and the acidity) were all lower in the leachates for those samples treated with the alkaline materials. Furthermore, the concentration decreases coincided with the increases in pH. However, the concentrations of manganese and iron were higher in the leachates from the treated samples, probably because these elements were leached from the codisposed materials themselves. None of the materials tested could produce acceptable leachates during the initial leaching of the sample. The same was true after regeneration of the waste pile by the passage of air through the waste. Therefore, codisposal of coal waste with these types of materials, at least by itself, is not likely to constitute a workable control technology. However, information gained from these studies will be useful in evaluating the effects of the mineralogy and underlying structure of potential disposal sites on the waste effluents. We are continuing these investigations in order to determine which types of soils or underburdens are the most beneficial and which are the most harmful to effluent quality.

The most widely used control technology for coal waste effluents is collection of the acidic drainages coupled with water treatment, usually alkaline neutralization. This approach is simple and uses proven technology. Also, cost analyses carried out in 1978 showed that this approach typically costs between 7 and 55¢ per ton of cleaned coal, so it is also relatively inexpensive. The obvious disadvantage is that the water treatment must be continued as long as the waste pile retains any acid-generating potential, which can be hundreds of years. Nevertheless, because this technique is so widely used, and because its principle, alkaline neutralization, is the same as that behind the best control technologies so far devised, additional investigation is warranted.

To study the chemistry of the neutralization process, we titrated a coal waste leachate with calcium hydroxide to various pH values and determined the concentrations of the trace elements left in solution. We then calculated the expected concentrations using a complex equilibrium code.[6] The calculated and experimental values compare well for the major cations [calcium, aluminum, Fe(II) and Fe(III)]. However, the behaviors of the anions of major interest (sulfate, arsenate, borate, and fluoride) are not well accounted for in the thermodynamic model, except for fluoride. In addition, the important trace element concentrations are all lower than the calculated values. We speculate that these elements (arsenic, cadmium, cobalt, chromium, copper, manganese, nickel, and zinc) are adsorbed on the hydrated iron and aluminum hydroxide precipitates. This behavior suggests that alkaline neutralization of coal waste leachates may actually be more effective in controlling the release of trace metal cations than thermodynamic calculations predict. Although these theoretical calculations cannot yet describe such complex chemical systems, they are valuable in identifying the factors controlling the solubilities of potential pollutants. Therefore, we will continue this line of investigation next year.

The formation of acid within the coal waste can be prevented in two ways. One is to dispose of the waste in an anaerobic environment (nonoxidizing) so that oxidation of the pyrite cannot occur. This is essentially a return of the coal waste to the type of environment from which it originally came. Disposal of the waste in this way is simple in principle, and once the anaerobic conditions are established, no further treatment is required to control the waste effluents as long as the disposal site is not disturbed. However, it takes a significant length of time to properly structure such a disposal site, and during this time, the acid generated within the pile must be controlled. We believe that combination of anaerobic disposal with a short-term method, such as the lime/limestone treatment, offers an acceptable solution to coal waste disposal.

The second way to prevent acid generation is to destroy the pyrite so that, even under oxidizing conditions, the waste has no acid-generating capability. In past studies we have shown that calcining, which destroys pyrite, is effective in controlling the leachabilities of the trace elements in high-sulfur coal wastes from the Illinois basin.[2-4] Calcining is a one-time, permanent treatment. Thus, the treated materials can be disposed of by conventional means without concern for their potential behavior in the distant and unforeseeable future. However, the calcining process merely exchanges one problem for another. The coal wastes are rendered innocuous because the calcining process drives off the sulfur, which eliminates the acid-generating capacity of the waste. The solids are left inert, but the evolved sulfur must be dealt with, either by flue gas desulfurization or by some technique of retaining the sulfur in the solid waste. Also, costs are high—not only for the control of the evolved sulfur, but also for the energy required to heat the mineral matter to the required temperatures. In fact, our cost studies show that the cost of calcining coal wastes can be as high as $10.00 per ton of cleaned coal (March 1978), clearly placing this technology beyond the realm of economic feasibility. Nevertheless, we recently conducted some experiments to determine whether waste from Plant K calcines in the same manner as that from Plant B. We found that trace element releases from Plant K mineral wastes, when calcined at the optimum conditions for Plant B, are not as well controlled. The discharge severities for manganese and nickel remained larger than unity after calcining, and significant discharge severities ($0.1 < DS < 1.0$) were observed for aluminum, copper, and iron. These results were quite unexpected in view of the similarity of the mineral make-up of the wastes. Conditions may have not been optimum for these wastes, or other factors may be involved, but we have not initiated the experimental program required to determine the reasons. We believe that, because the treatment is very expensive, additional intensive study is unwarranted.

II. ASSESSMENT OF HIGH-SULFUR APPALACHIAN COAL WASTES

During the past year we have systematically studied the refuse from two coal cleaning plants located in western Pennsylvania. These plants, designated Plants I and K, process high-sulfur Appalachian coal, although they use different processes. The laboratory work has been completed for both plants, but because the data are complete only for Plant K, the results for Plant K are presented in this report; results for Plant I will be presented in the next annual report. Plant K is a jig operation and is unusual among the plants we have studied because the fines are not cleaned, but are sent straight through the plant and combined with the clean coal. Consequently, the plant output consists of cleaned coal, coarse mineral matter, and a 60-mesh slurry effluent. In this study, we have examined only the coarse refuse, the cleaned coal, and the raw feed coal.

In general, the mineral content of the waste from Plant K is comparable to that previously studied from the Illinois Basin. The Plant K material has a slightly lower sulfur content, but slightly higher concentrations of lithium, chlorine, arsenic, cadmium, antimony, and lutetium. Except for zinc and rubidium, which are slightly lower in the Plant K waste, all the remaining elements are present in comparable concentrations. No marcasite was detected, but the pyrite concentrations ($\sim$25%) are typical of the high-sulfur coal wastes we have studied. In addition we identified the presence of siderite ($FeCO_3$). This is the first time we have found this mineral in coal wastes. The calcium content of the Plant K refuse is low, which suggests that little or no calcite is present. This material has little or no self-neutralizing capacity.

Before chemical and mineralogical analyses, the refuse from Plant K was separated into seven fractions, based on the gross external appearances of the various pieces. Examination of these fractions along with the composite waste permitted us to derive some very useful information about the relationships between some of the trace elements and the various mineral phases. Most of the leachable trace elements tend to concentrate in those fractions containing the highest concentrations of clays and other silicate minerals. However, certain elements (selenium, arsenic, antimony, cadmium, and iron) are associated with the pyritic minerals. These elements are undoubtedly present in the form of sulfides (or selenide) and some of them are important because of their toxicological properties. Leaching studies (described below) suggest that the chemistry of these elements in the waste pile effluents is somewhat different than that of the rest of the trace elements.

We performed micromineralogical studies of these coal wastes, using electron microscopy coupled with energy dispersive spectrometry. Because this technique observes such a small fraction of the sample at any one time, the results must be interpreted carefully. Nevertheless, one can perform elemental analyses while retaining the spatial resolution of the microscope. This is difficult, if not impossible, with other techniques. These studies confirmed our observations that most of the trace elements are associated with various types of clays. In addition, the trace elements seem to be present as discrete mineral phases, rather than in chemical associations with the gross minerals.

We performed static leaching experiments in which the coal waste was shaken with deionized water for varying lengths of time ranging from 1 to 50 days. The mixtures were then filtered and the filtrate was analyzed for acidity, specific conductance, and trace element content. All these measurements increased with leaching time. In many cases, the leachates were very acidic, with pH values less than 2, indicating that this waste could generate drainages of environmental concern. Iron, arsenic, nickel, manganese, and aluminum had discharge severities greater than unity, indicating sufficient concentrations in the waste effluents to be of environmental concern. Zinc, cadmium, and copper had discharge severities between 0.5 and 1.0, suggesting that these elements may be cause for concern under certain circumstances.

The concentrations of several trace elements increase sharply with increased time, and they continue to increase even after most of the other elemental concentrations have reached steady-state values. These elements, arsenic, selenium, and cadmium, are associated with sulfide mineral phases, possibly as sulfides (or selenide). We surmise that the mobilization of these elements depends not only on the pH of the leachate, but also on the rate at which the respective mineral phases are oxidized.

In addition to the static leaching experiments, we also performed a series of dynamic leaching experiments with the coal wastes by placing the coal waste into glass columns and pumping deionized water through the columns at a slow and constant rate. The effluents from the columns were sampled and analyzed periodically for acidity, specific conductance, and trace element concentrations. After all these values had reached steady state, the leachate flows were stopped for 2 weeks and air was forced through the columns. The leachate flows were then resumed and the experiment continued as before until the trace element concentrations in the effluents again reached steady state. This experiment is designed to simulate the weathering of an uncontrolled waste pile that is intermittently exposed to wet (rain) and dry cycles. The initial leachates are very acidic when they emerge from the waste column, with pH values from 1.9 to 2.2. As the leachate flow continues, these decay to more moderate values (~4). After the columns are "regenerated" by passing air through them, the initial pH values are again very low (~2.3 to 2.4). Continuation of the leachate flow also causes these values to decay to moderate steady-state values (~4). Trace element concentrations behave in exactly the same way as the solution acidity (Fig. 2). This behavior can be explained in the following way. Before the experiment the coal waste is exposed to air in the normal course of handling and sample preparation. This causes some oxidation to take place. The oxidation of pyrite within the waste leads to the formation of sulfuric acid, which accumulates in the waste until it is washed out by the leachate early in the leaching experiment. As the leaching proceeds, both the acidity and the trace element concentrations decay to more moderate steady-state values. However, when the leachate flow is interrupted and air is forced through the column, oxidation again takes place and the resulting acid accumulates in the waste until leaching is resumed. Thus when water is again allowed to flow through the column, the initial effluents are very acidic and the trace element concentrations are very high. Our observations

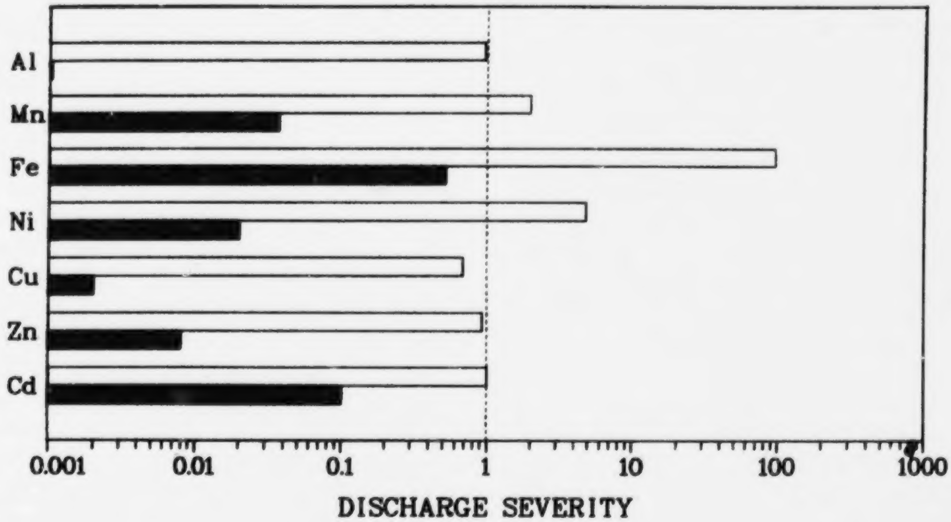

Fig. 2.

Discharge severities (leachate concentration/100 × MATE) for selected trace elements in leachates from Plant K coal preparation wastes as determined by dynamic leaching experiments—initial values (unshaded) and steady-state values (shaded).

of very acidic leachates after air regeneration of the waste column suggest that this waste has strong acid-generating tendencies, and that the acid-drainage problem associated with this waste, significant even under steady-state conditions, is aggravated when the leaching is done intermittently.

The initial discharge severities of iron, nickel, and manganese were all greater than unity, but iron, with a discharge severity of more than 100, was by far the worst offender. In addition, zinc, cadmium, aluminum, and copper had initial discharge severities between 0.5 and 1.0. These elements may pose problems of environmental concern under certain weathering conditions. In past reports in this series, we showed that trace element concentrations in the leachates are controlled by the pH. However, in certain cases (lead, arsenic, and possibly cobalt and aluminum), other factors are involved. The most important of these is probably oxidation of the respective minerals containing these elements.

In summary, the experimental evidence seems to indicate that the high-sulfur waste from Plant K may pose problems with serious environmental consequences unless it is properly disposed of. These problems are caused by the high acidities and the high concentrations of several trace elements in the waste effluents. Although our laboratory leaching conditions may be somewhat more severe than those encountered in a large waste pile, it is clear from our field work that there is cause for concern in the disposal of these solid wastes. The behaviors of these materials exactly parallel those of the high-sulfur wastes from the Illinois Basin.[1-4] While there is every reason to believe that the same control technologies will work for each of these coal wastes, we plan to test some of the more promising techniques with this waste as well as that from plants in the Illinois Basin.

III. LEACHING PROCEDURES

Throughout our investigation of coal waste, we have attempted to devise leaching tests that provide meaningful information on the environmental behavior of these materials. Accordingly, we have developed several procedures and have used the results of these tests as the basis for our predictions on the weathering behaviors of coal cleaning wastes. However there remains the question of how these procedures compare with those used by other researchers and, in particular, how they relate to the EPA extraction procedure used to classify wastes under the Resource Conservation and Recovery Act (RCRA). We addressed this question by comparing the results of our leaching procedures to those obtained using the EPA extraction procedure.

Seven mineral wastes from coal preparation plants in the Illinois Basin, the Appalachian region, and the Western US were leached in accordance with the EPA extraction procedure published in the Federal Register dated May 19, 1980.[7] This amounts to using 100 g of waste, ground to pass through a 9.3-mm standard sieve (-3/8 in.), adding 1600 mℓ of deionized water to the waste, and agitating for 24 h in an extractor designed to ensure that all sample surfaces are continuously brought into contact with well-mixed extraction fluid. The pH values of the mixtures are monitored during the extraction and, if the pH is greater than 5, adjustment must be made by addition of 0.5*N* acetic acid. After 24 h, the solids are removed by filtration, and the concentrations of eight elements (Ag, As, Ba, Cd, Cr, Hg, Pb, Se) in the filtrate are determined.

The primary differences between our leaching procedures and that prescribed by EPA are the use of a higher liquid-to-solids ratio in the EPA test, the examination of a different set of elements by the EPA test, and the requirement that alkaline systems be acidified in the EPA procedure. Compared to leaching tests that we have used over the past several years in our research on coal wastes, the results of the EPA procedure compare favorably with those of our procedures for elements examined by both.

Among the samples that we leached according to the EPA procedure, only the western coal waste required addition of acetic acid to maintain the pH below 5. Judged according to the criteria in the Federal Register, all the coal waste leachates had trace element concentrations below the maximum values set by EPA. However, two factors should be noted. First, iron, aluminum, nickel, and manganese, the most important elements in coal waste leachates, are not included in the protocols at the present time. Second, we believe that the acidification of neutral or alkaline materials simulates an abnormal environment for these samples, and is inappropriate for coal wastes.

RESULTS AND DISCUSSION

I. ENVIRONMENTAL CONTROL TECHNOLOGIES

A. Codisposal Techniques

1. Treatment with Lime and/or Limestone. One major conclusion from our earlier studies of the environmental behavior of coal refuse materials concerned the importance of pH in controlling trace element releases during refuse leaching. In every case in which leachate pH was maintained at or near the neutral point, only minimal amounts of trace elements were solubilized by the leachates. Conversely, when oxidative degradation of the pyritic materials in the refuse caused leachate acidities to build up, substantial quantities of aluminum, manganese, iron, cobalt, nickel, and copper were released in the acid leachates. This marked dependence of trace element contamination on leachate pH suggested that a potentially valuable way to prevent trace element releases from discarded refuse materials might be to add neutralizing agents to the refuse before disposal to negate leachate acidity as it is formed. We performed several experiments in which lime or crushed limestone was mixed with or placed adjacent to high-sulfur coal waste to observe the leaching behavior. These experiments, described in Ref. 3, showed this approach to be effective under the right conditions.

We showed that the use of hydrated lime can control the effluent pH and is only moderately costly.[1] For example, levels of 0.5 or 1.5% of lime were too low to neutralize the acid in high-sulfur coal waste from Plant B. However, levels of 3 and 10% yielded acceptable leachates over the duration of the experiment. Long-term effectiveness was not addressed in this experiment.

Similar experiments were done to assess the use of crushed limestone. Limestone crushed to −3/8 in. was only partly effective in raising the pH of the leachates from high-sulfur coal waste. Two possible reasons are (1) Limestone alone cannnot elevate solution pH to very alkaline levels because of its insolubility and because, once solubilized as bicarbonate, it tends to form a buffer system at slightly acid pH. (2) More important, however, is that calcium carbonate is insoluble except under acid conditions, so that its neutralization of the leachate is slow unless the leachates are very acidic. If, in fact, the effectiveness of limestone is limited by its rate of dissolution, results should be improved by using powdered limestone instead of crushed limestone because of the greater surface area.

In addition to direct admixture of lime or limestone to the coal waste, we also added excess lime (5% in water) and then neutralized it with CO_2. The rationale was that the excess lime should neutralize the acid initially present while CO_2 precipitates the remainder as a durable coating of $CaCO_3$ on the coal waste particles. This coating would then serve the dual purpose of neutralizing any new acid generated and also act as a barrier to incoming oxygen, so that further oxidation of the waste and the resulting acid generation would be retarded. This procedure was successful in controlling both the acid and the trace element contents of the leachates.[1] However, the need to add large amounts of gaseous CO_2 to a coal waste slurry makes this scheme impractical on any realistic scale.

A simpler neutralization and coating scheme would be to sequentially add a small amount of lime, followed by a large amount of powdered limestone as a slurry. This could achieve control of leachate acidity and should be much easier to implement on a large scale than any scheme requiring neutralization by CO_2. We performed a long-term experiment in which we examined the leachates from high-sulfur coal wastes mixed with various levels of lime and one mixed sequentially with lime and limestone. Preliminary results of this experiment are reported in Ref. 4, which includes partial results from the first 12 weeks of the experiment. In the following discussion, we detail complete results of the 10-month experiment.

A highly acidic Illinois Basin coal waste was mixed in plastic-lined 5 gal. barrels with wet slurries containing lime in amounts from 0.17 to 3.3 wt% of the waste. In one case, 1.1% limestone slurry was mixed in after 0.33% lime had been used. These slurries were screened to remove excess water and placed in specially designed disposal boxes. Six boxes of each of the six lime/limestone/waste mixes were then placed in a pattern to await wet and dry weathering cycles.

The weathering cycles consisted of weekly additions of water equivalent to 3/4 in. of rain, which was drained from each box 24 h later and immediately analyzed for pH, specific conductance, and iron species. Sample aliquots were acidified and retained for trace element analyses to be conducted after the completion of the experiment. The procedural details of this experiment are reported in Ref. 4.

Figure 3 shows the pH values of the effluents as a function of the weathering time. The lime added raised the initial pH above 5 in all cases; however, the pH values all dropped to below 4 after only 3 weeks, except for the sample with the most lime and that containing limestone. In the sample with the most lime, pH values were unacceptably high in the beginning. Clearly, lime is an effective neutralizing agent, but it does not maintain high pH values for extended times because, first, excess lime is washed out of the system by water percolating through the waste, and second, oxidation of the coal waste is not retarded in any way. As soon as the neutralizing capacity of the resident lime has been exhausted the pH drops to levels typical of untreated coal waste effluents.

Treatment of the waste with lime followed by a limestone slurry was much more effective in controlling the effluent pH: the pH remained between 7.3 and 7.6 for nearly 4 months. The inability of the limestone to generate strongly alkaline pH values is a distinct advantage, and because it is insoluble, it does not wash out of the waste easily. Whether the limestone coating actually retards the oxidation of the waste or whether it simply neutralizes the acid as it is generated is debatable; it is effective in controlling pH, whatever the mechanism, for a significant period of time. Although this treatment is not permanent, it may be useful as part of a more comprehensive disposal scheme.

Figure 4 shows the total iron contents of the effluents as functions of time. The iron values closely parallel the effluent acidities; that is, when the acidity is high (low pH) the iron contents of the leachates are high. When the acidity is low (high pH) the iron concentrations in the leachates are also low. Sample 6, the lime/limestone-treated material, is particularly interesting because the iron levels remain low as long as the pH is maintained in the neutral region. Consequently, this treatment effectively controlled the pH and the release of iron for nearly 4 months.

In addition to iron, a number of other elements must be considered. Figures 5 through 10 show the behaviors of nickel, aluminum, manganese, copper, zinc, and cobalt. Note that these plots are logarithmic; the actual concentration ranges involved are much larger than they appear. In every case, the behavior is the same. When acidities are low, the concentrations of these elements in the leachates are also low. Again, control of the pH is a key to control of the leachate quality. More important, however, the lime/limestone slurry treatment maintained acceptable effluent quality for a period of months.

Figure 11 shows the calcium contents of the leachates as functions of time. The calcium concentrations are consistently high in all samples. Presumably, the acid generated within the waste dissolves the calcium compounds, thereby releasing the calcium. Because the major calcium components, lime or limestone, were added in substantial amounts, the calcium releases are predictably large. The behavior of sample 6 is again very interesting. If retarding the oxidation of the pyrite in the coal waste (by the formation of a coating around the coal particles) is a major factor in controlling the acidity of the leachates, there should be a substantial reduction of the calcium release from the sample while this mechanism was operative. In fact, sample 6 does show a reduction in the calcium release during the first 4 months, but this reduction is not very large, so other important factors must be involved. We conclude that the major factor in controlling the effluent pH is probably the neutralization of acid as it is formed in the waste. If this is true, the major difference between the lime/limestone treatments and the simpler lime treatments is that the limestone is more durable and not easily washed out of the system. Thus the treatment should be effective for a longer period of time than a simple lime treatment.

Although the degree of control offered by the lime/limestone slurry is certainly encouraging, the main point is whether the leachates are harmful to man or the environment. To determine this, we compared the trace element contents of the leachates to the Multimedia Environmental Goals (MEG) that have been set forth by the Environmental Protection Agency.[5] Discharge severities were calculated by finding the ratio of the observed trace element concentration to its corresponding adjusted ecology Minimum Acute Toxicity Effluent (MATE) value.[5] The MATE values, derived from various types of toxicological data, are meant to represent levels of various chemical moieties above which deleterious health or ecological effects might occur. The MATE values were adjusted to account for dilutions of the waste effluent by multiplying the published MATE value by 100 before calculating discharge severities.* Thus, very

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*This dilution factor was recommended by Garrie Kingsbury of Research Triangle Institute.

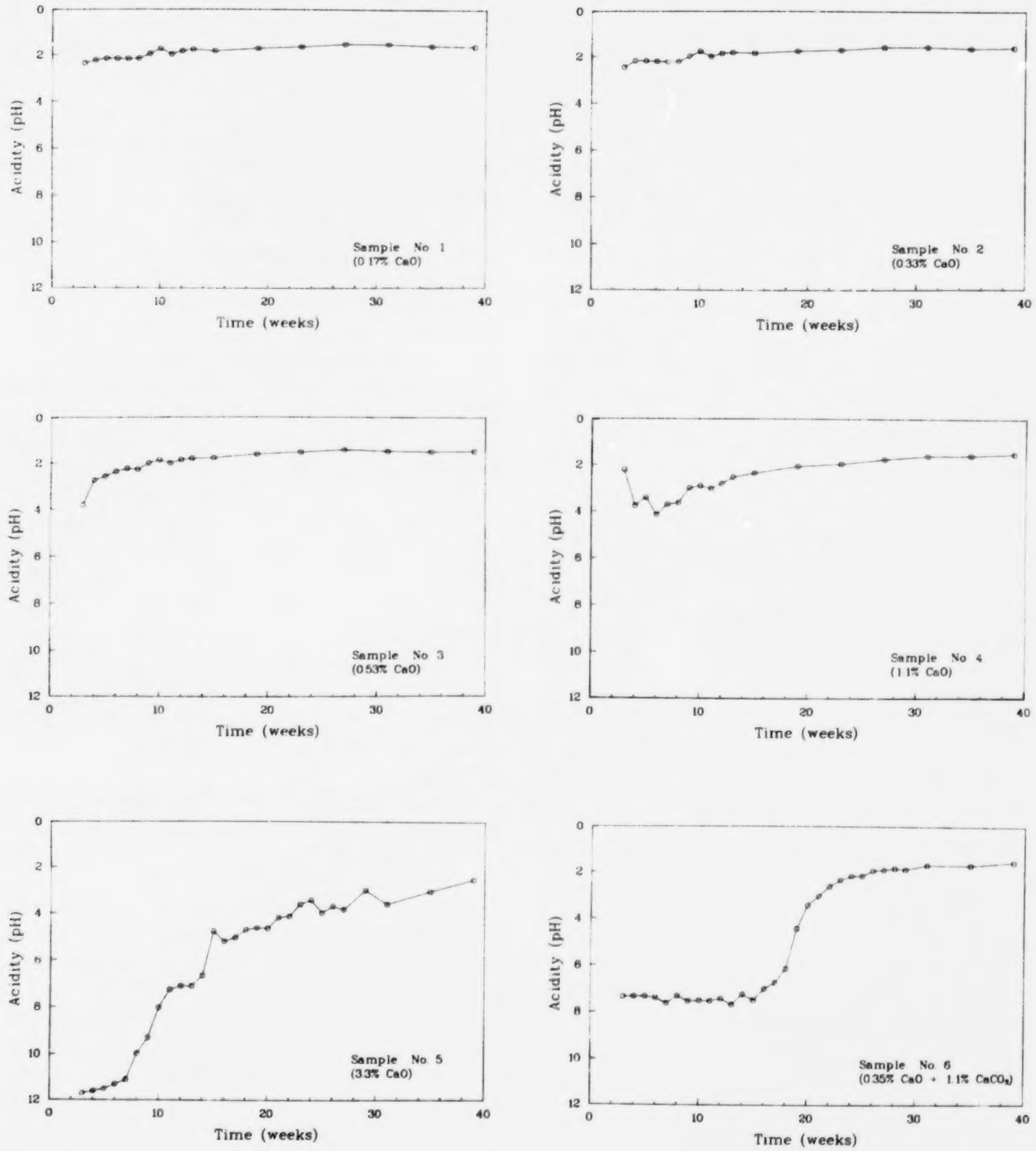

Fig. 3.
Dependence of effluent pH on time for six treated coal waste samples.

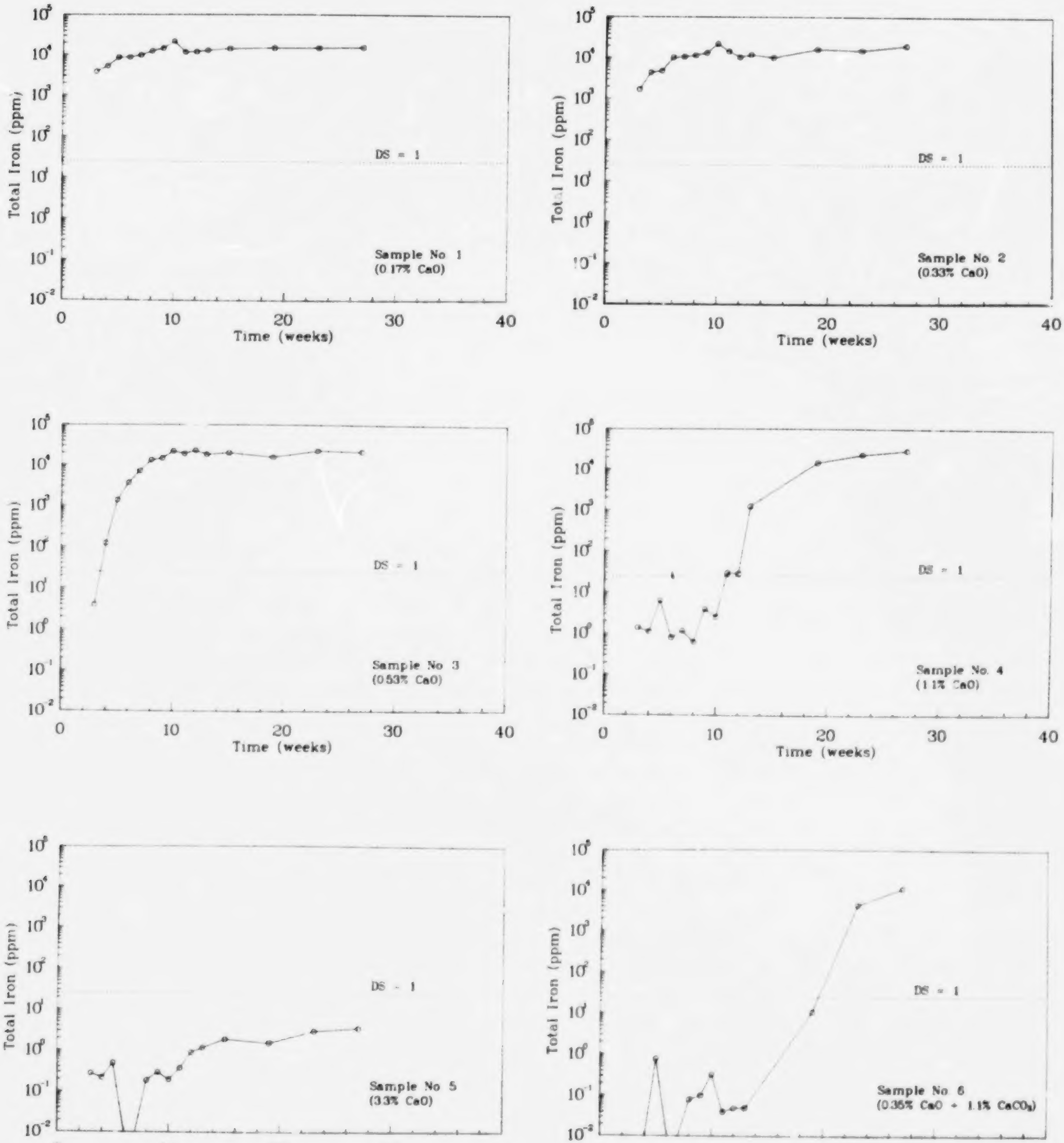

Fig. 4.

Concentrations of iron in the effluents from six treated coal waste samples as functions of time.

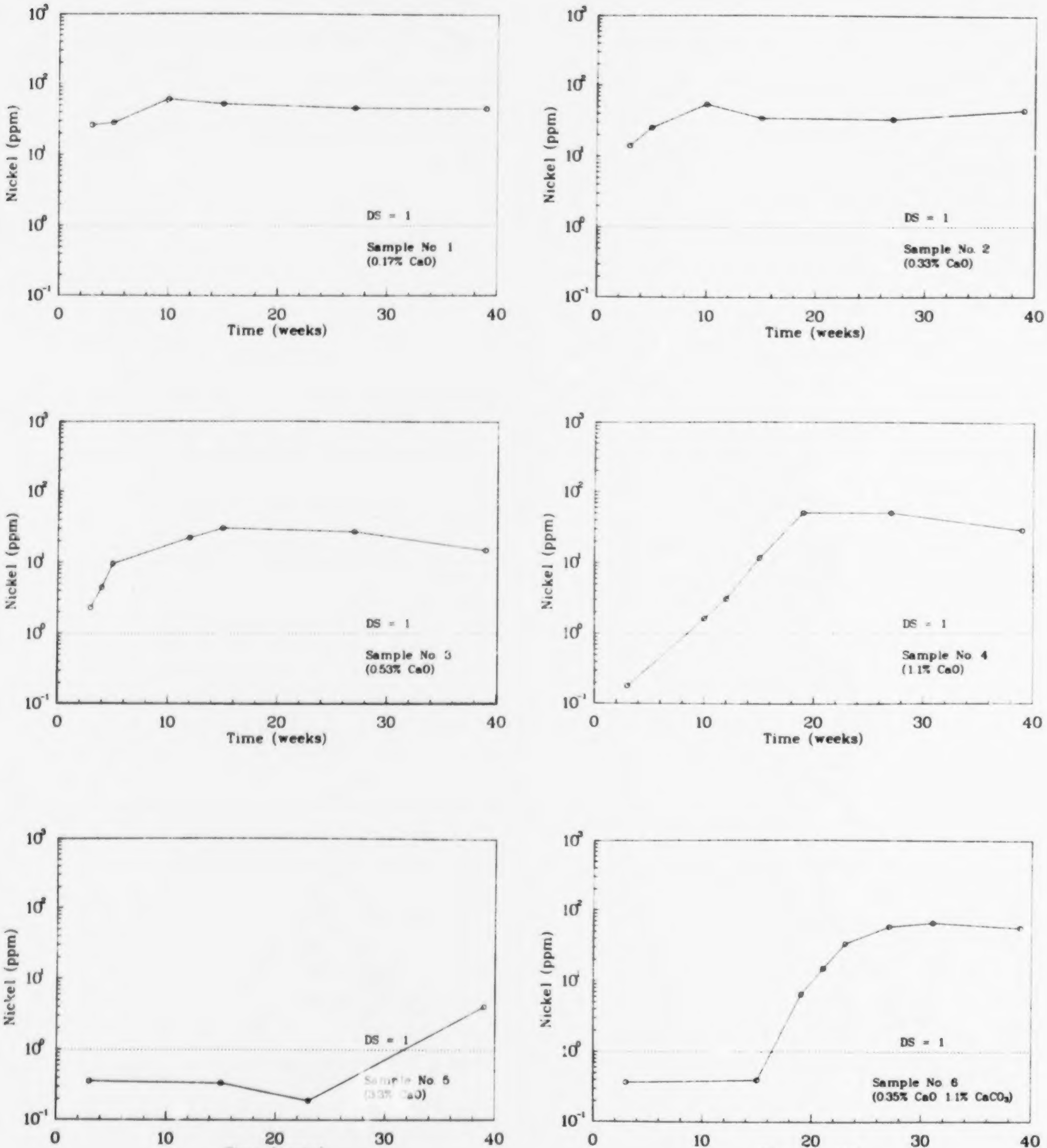

Fig. 5.
Concentrations of nickel in the effluents from six treated coal waste samples as functions of time.

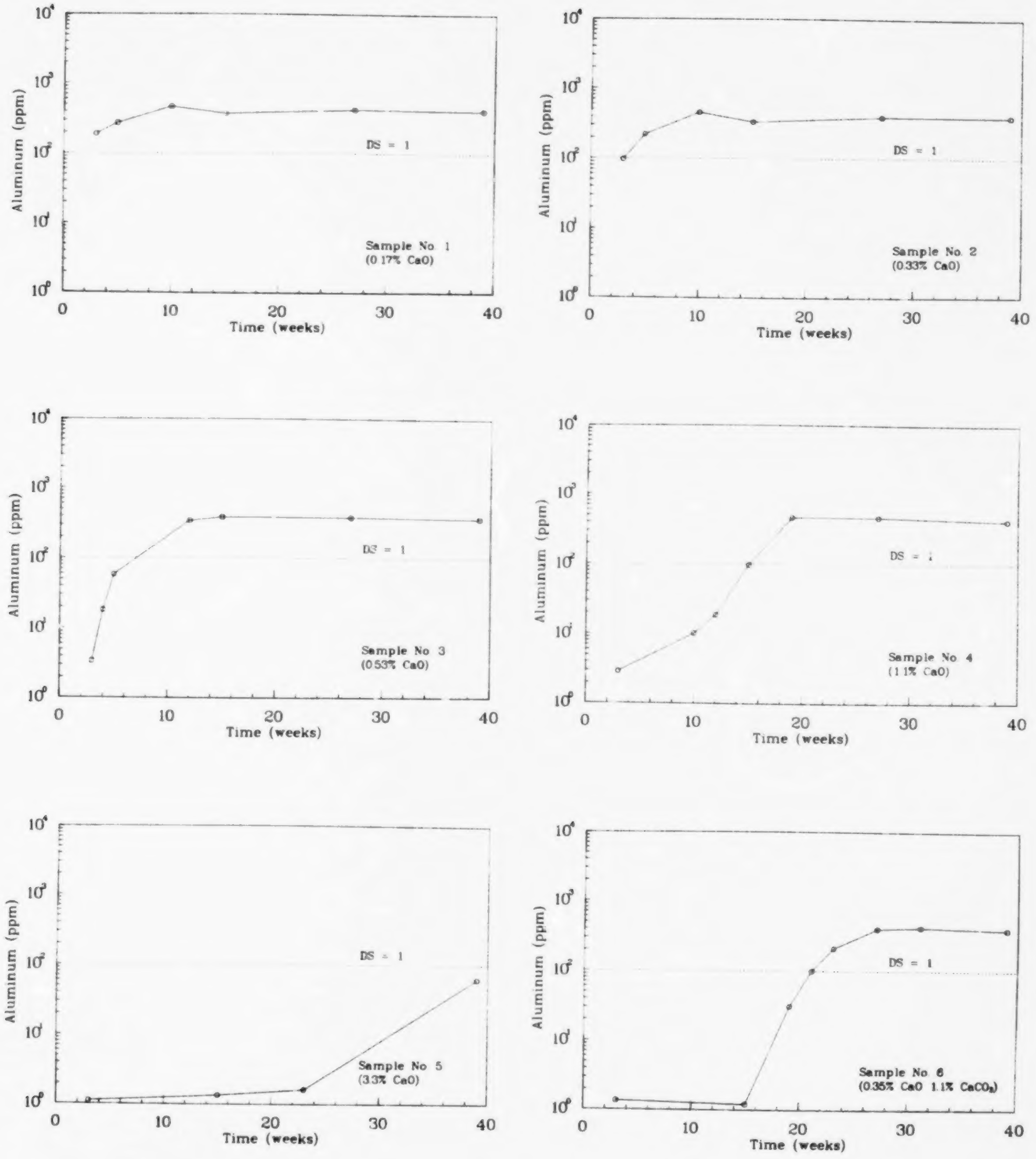

Fig. 6.
Concentrations of aluminum in the effluents from six treated coal waste samples as functions of time.

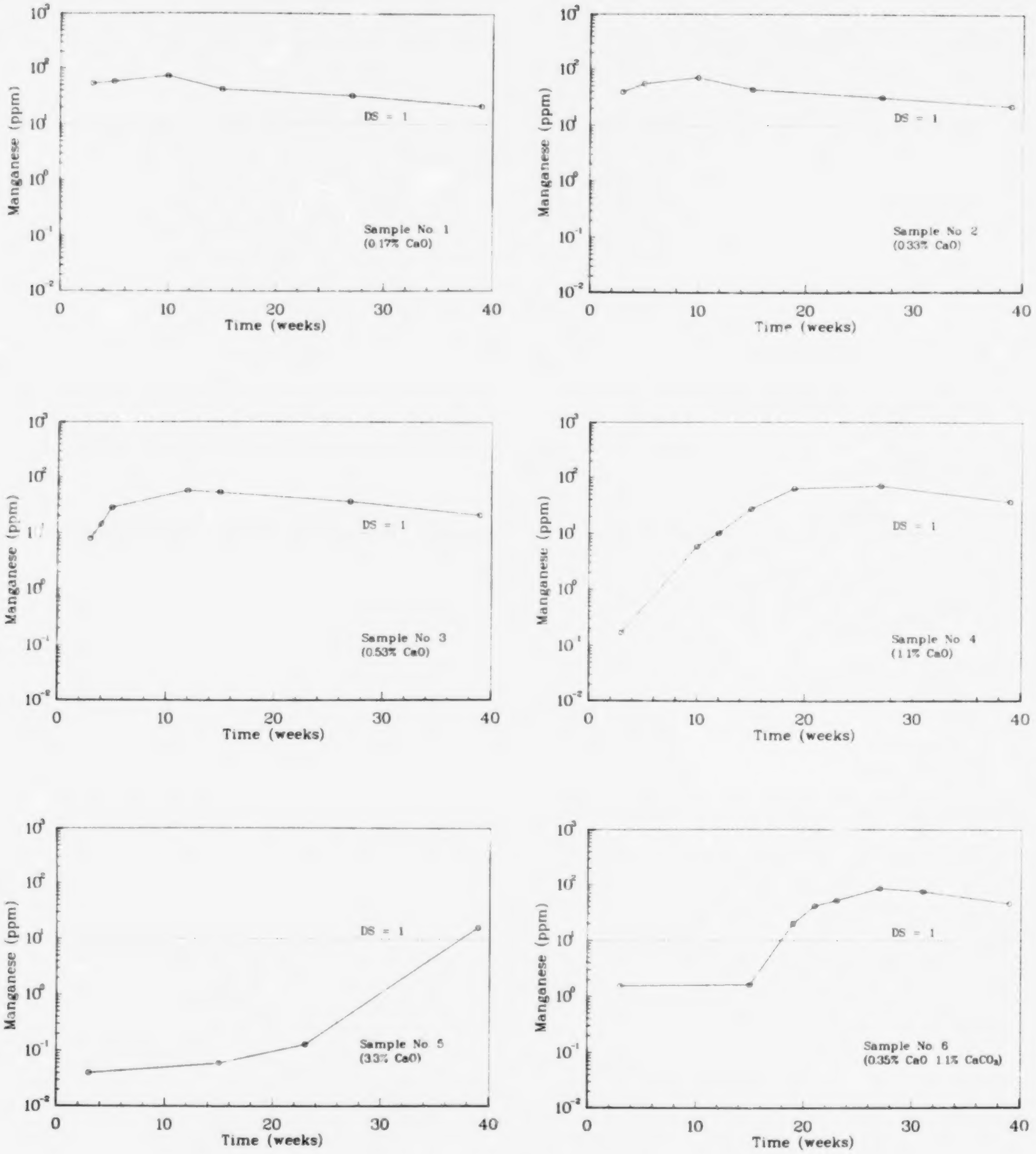

Fig. 7.

Concentrations of manganese in the effluents from six treated coal waste samples as functions of time.

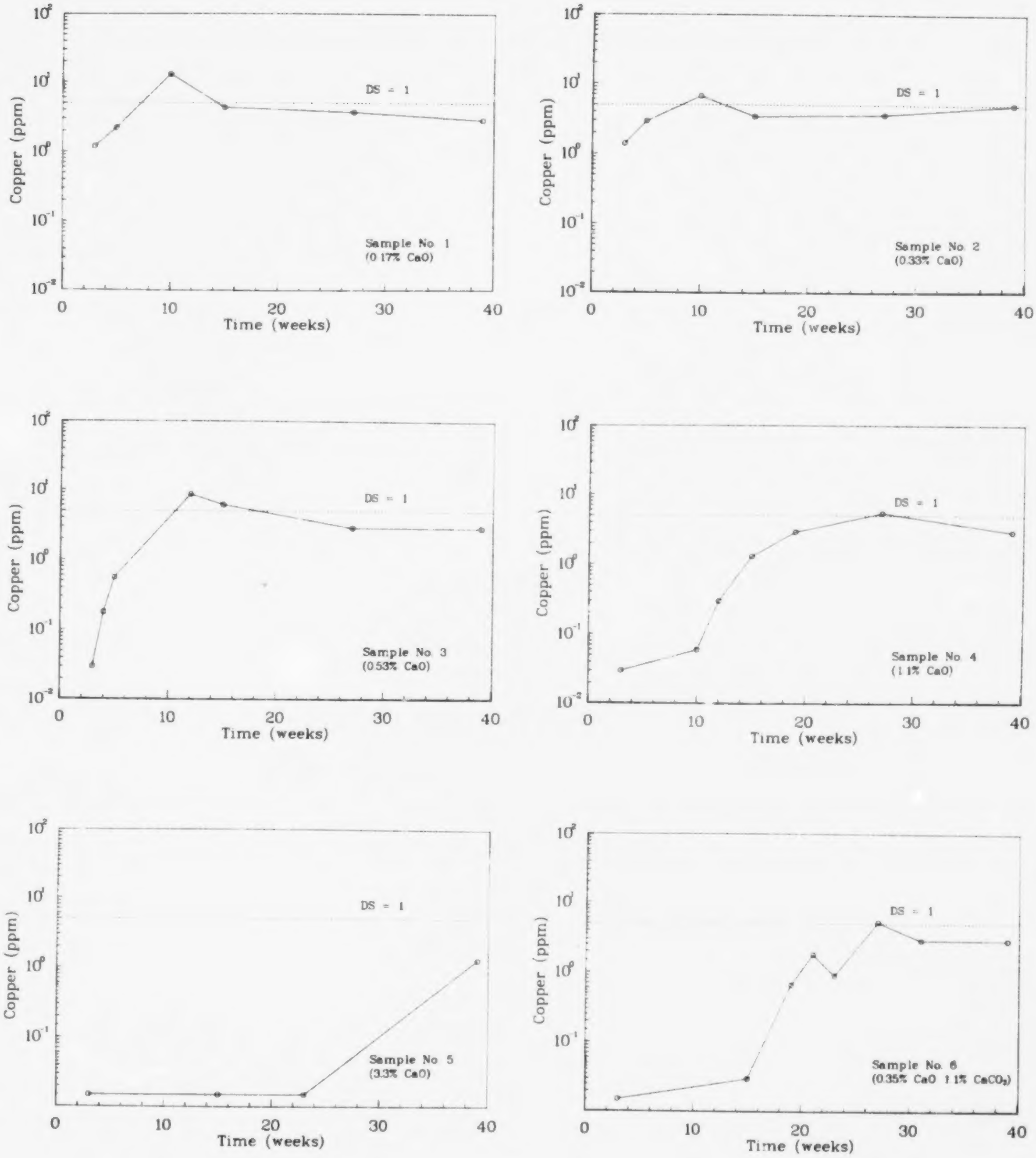

Fig. 8.
Concentrations of copper in the effluents from six treated coal waste samples as functions of time.

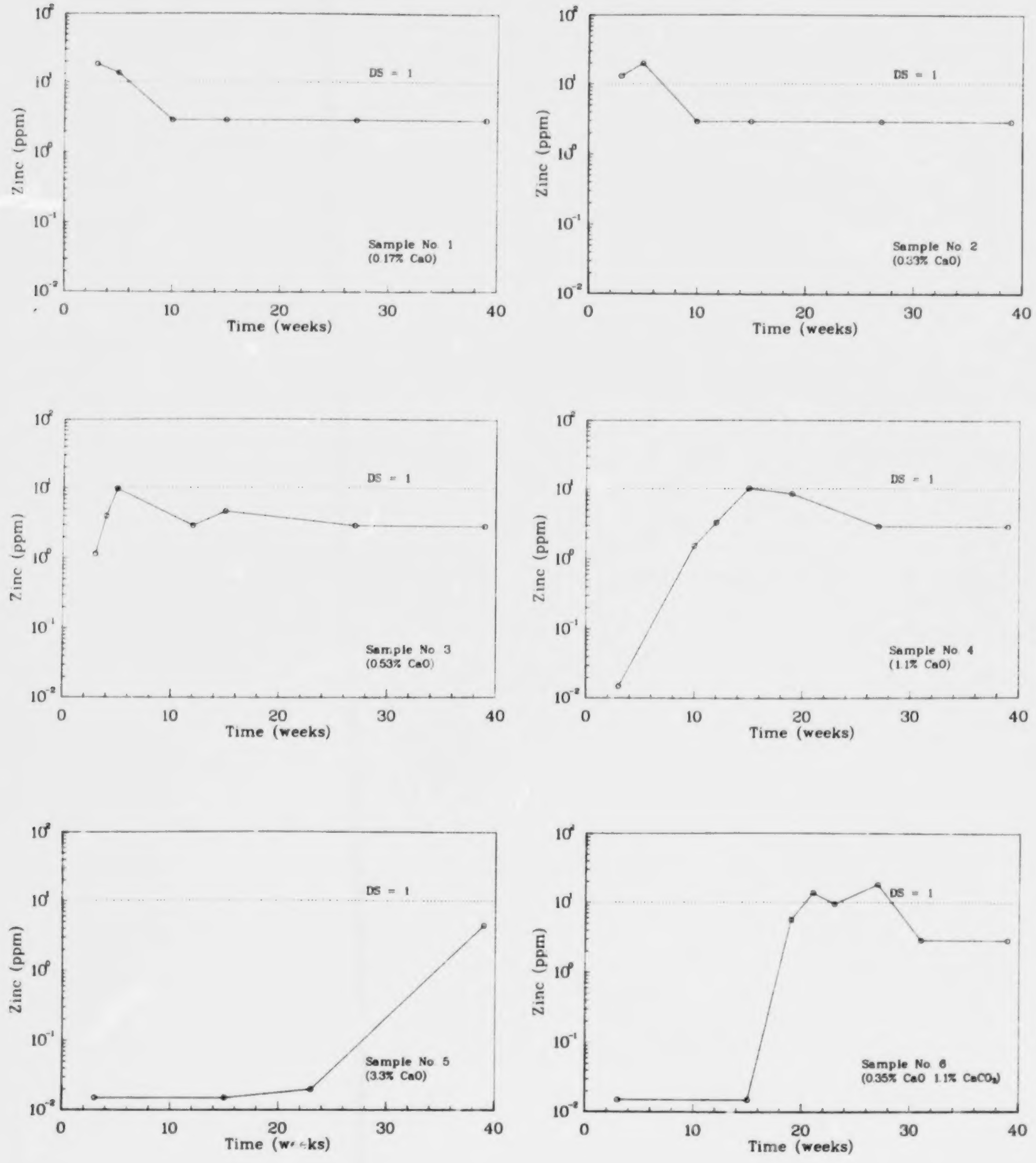

Fig. 9.
Concentrations of zinc in the effluents from six treated coal waste samples as functions of time.

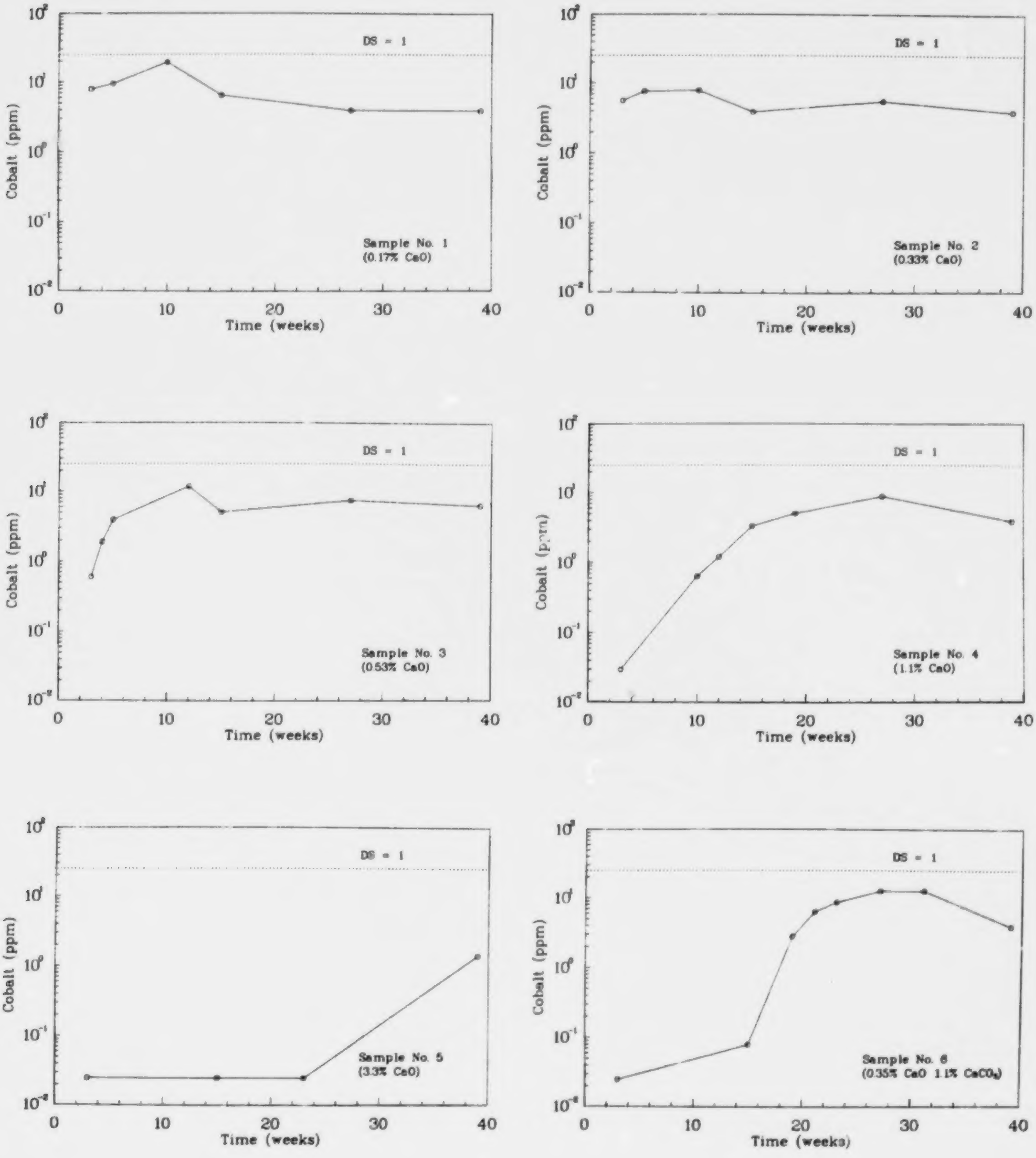

Fig. 10.
Concentrations of cobalt in the effluent from six treated coal waste samples as functions of time.

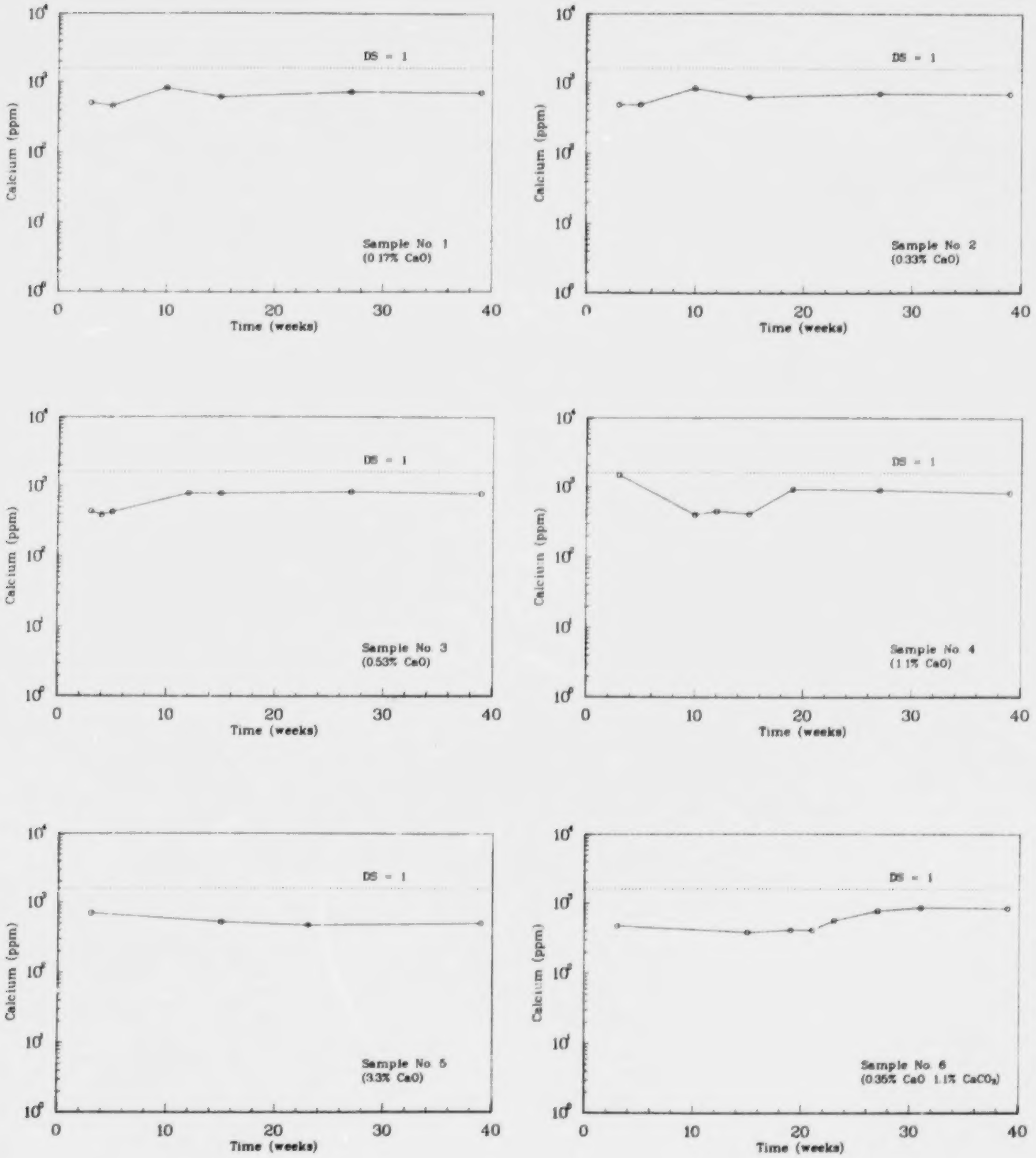

Fig. 11.

Concentrations of calcium in the effluents from six treated coal waste samples as functions of time.

small discharge severities are desirable, whereas those near one or larger may be cause for concern. The horizontal dashed lines in Figs. 3 through 11 show the levels at which the discharge severities are equal to unity, a simple way to note when the leachates are of acceptable quality. (A complete table of discharge severities is included in Appendix A.) The lime/limestone treatment maintained acceptable discharge severities for all trace elements for 4 months. The sample treated with the most lime also had acceptable discharge severities for a longer period, but the leachates from this sample were strongly alkaline during the early parts of the experiment.

Because the pH seems to be the major controlling factor in trace element leachability, we examined the functional dependence between the concentration in the leachate and the pH for each element. The results of these comparisons are shown in Fig. 12. All data from the six samples are plotted, regardless of the time or the treatment process. In spite of the large variations in conditions among the samples, the correlations are very good, particularly for the elements present in high concentrations, which permit better analytical precision. These results should be compared with calculated values derived from complex equilibrium codes, but at present, the solution pH is apparently the major controlling factor for the effluent quality.

In summary, the lime/limestone sequential treatment of high-sulfur coal wastes has some attractive features. It seems to be very effective, at least for some months, and, as we showed in our previous annual report,[4] it is among the less expensive options. Its major negative aspect is that it is not permanent. Also, there are several unanswered questions. For example, is this treatment effective with different types of coal wastes? What are the effects of freeze-thaw cycles? What about the possible effects of compaction of the waste pile? Are there better treatment conditions: what are they? In spite of these limitations and uncertainties, we consider this type of treatment to be one of the best options available at present, particularly as a part of a more comprehensive disposal strategy. We are continuing to investigate this approach to more thoroughly understand its limitations and to optimize its performance.

2. Codisposal with Soils or Process Wastes. Previous batch experiments have shown that natural materials, such as subsurface soils and mine overburden, have a considerable potential for reducing acidity and contaminant concentrations in leachates from coal cleaning wastes.[4] Another possible disposal scheme that could mitigate the escape of contaminated leachates from coal cleaning waste disposal sites is disposal along with natural or process waste materials. This might involve dumping coal cleaning waste and alkaline material together and mixing them by conventional tillage procedures. The acidity of the waste would be neutralized *in situ*, thereby producing a less contaminated leachate by precipitation of insoluble solids. In addition, because many soils have significant adsorption capacities, secondary control by adsorption of chemical species not precipitated by alkaline neutralization is probable. A variation of this procedure consists of preparing or selecting a site that can be underlain by subsurface soil or mine overburden materials with desirable physical and chemical properties. Such materials, with adequate permeability, alkalinity, and adsorption capacities, could greatly reduce contaminant concentrations in leachates from coal waste piles, if the leachate were made to percolate slowly through them.

Two sets of experiments were completed during FY 1980 to investigate the possibility of soil-waste codisposal as a control measure. The first was a preliminary experiment using mine overburden. In the second experiment, several soils were mixed with coal cleaning waste and leached in columns with water to determine contaminant concentrations compared with a control column containing only waste. The geologic materials used and some of their physical, chemical, and mineralogical properties are listed in Table I and Appendix B, Table B-I. The materials were all collected from the Illinois Basin at or near active coal mines. The materials were air dried, crushed to −3/8 in. with a jaw crusher, and subsampled using a sample splitter.

a. Experiment A: Attenuation of Acidity and Trace Elements by a Calcareous Mine Overburden. This experiment was designed to investigate three possible treatments for acidity and trace element attenuation by a mine overburden collected above Kentucky coal seam 11.

For the first treatment, we used a mixture of 422 g of −3/8-in. coal cleaning waste and 278 g of −3/8-in. soil. We used enough soil to neutralize 150% of the acidity in the coal waste. Acidity was determined by titration of

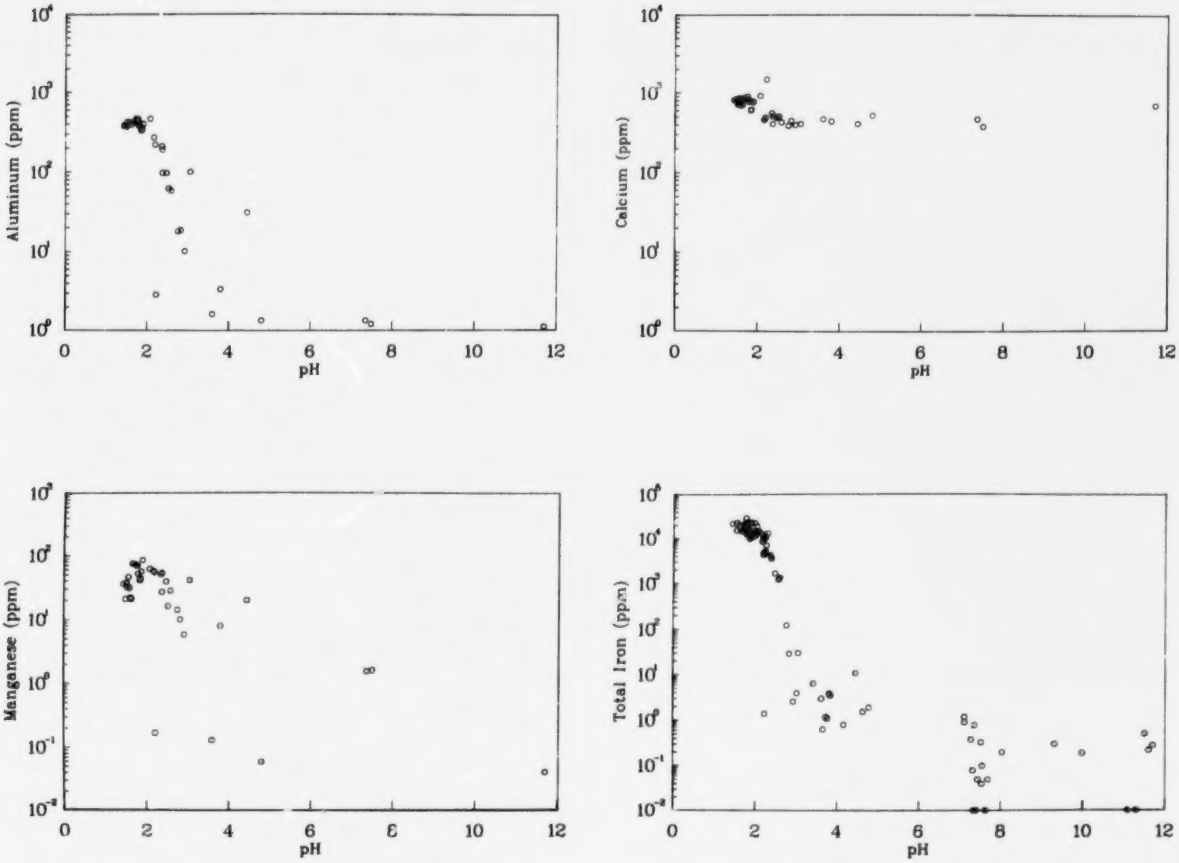

Fig. 12a.

Concentrations of selected trace elements in treated coal waste effluents vs pH.

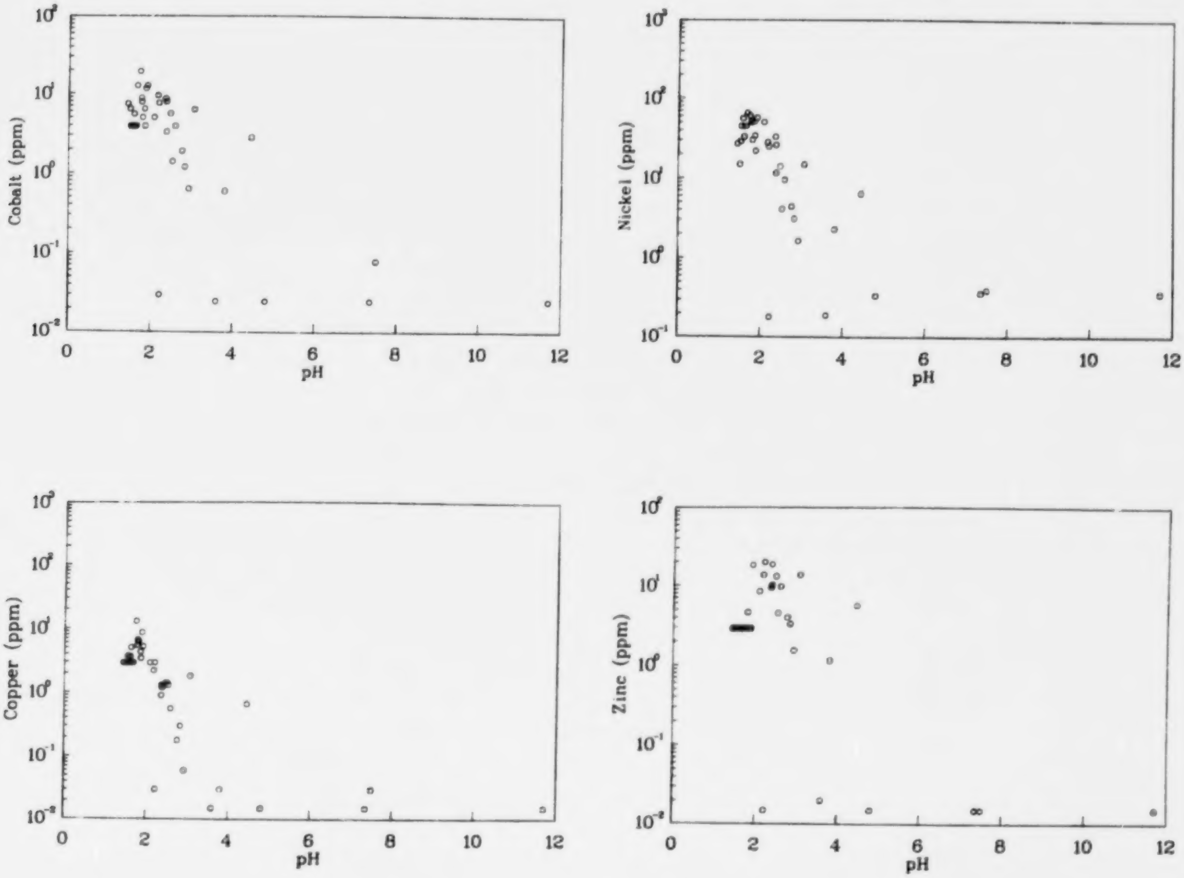

Fig. 12b.
Concentrations of selected trace elements in treated coal waste effluents vs pH.

TABLE I

PHYSICAL AND CHEMICAL PROPERTIES OF MATERIALS USED IN ATTENUATION AND CODISPOSAL EXPERIMENTS

	pH[a]	Carbonate[b] (%)	Organic Matter[c] (%)	Cation Exchange Capacity[d] (meq/100g)	Free Iron Oxides[e] (%)	Clay[f] (%)	Particle Size[g] (mm)
Seam 11 Overburden	7.6	3.8	3.2	9.8	1.4	0	0.21
Seam 12 Overburden	7.8	1.4	3.2	7.5	2.5	9.5	0.18
Acidic Loess Subsoil (OKAW)	4.8	0.5	1.5	24.1	0.8	22.0	<0.074
Calcareous Till Subsoil (BS3)	7.9	7.1	0.1	14.5	3.5	28.6	0.17
Quarry Limestone (Ill)	7.5	–	–	–	0	–	0.15

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[a] pH made on filtrate after 16 h water-soil equilibration on shaker at 2:1 water:soil ratio.

[b] Carbonate by rapid titration method.

[c] Walkley-Black.

[d] Ammonium acetate extraction following saturation with sodium acetate.

[e] Sodium-dithionite extraction.

[f] Pipet sedimentation.

[g] Mass-median diameter by sieve analysis.

waste leachate. Soil alkalinity was based on titratable carbonate (Table I). Codisposal with −3/8-in. soil should be feasible because such sizes can be realized at field sites.

For Treatment 2, we used the same mixture and capped it with 92 g of the same soil ground to a mass median diameter (MMD) of 0.21 mm. Water first flowed through the soil-waste mixture and then through the finely ground soil cap.

Treatment 3 consisted of 422 g of −3/8-in. waste topped by a 278-g layer of ~20- to 50-mesh soil (MMD = 0.21 mm). (No soil was mixed with the waste for this case.) Water first flowed through the waste and then through the finely ground soil.

Treatment 4 consisted of 422 g of −3/8-in. waste as a control.

All columns were leached for 21 days with deionized (Milli-Q) water at 10 mℓ/h until 5 ℓ had passed through each. Flow was directed upward. The column, influent water, and effluent leachate were maintained under an argon atmosphere throughout in an attempt to prevent oxidation of Fe(II) to Fe(III). We monitored Eh, pH, conductivity, Fe(II), and total dissolved Fe throughout. After leaching stopped, water-saturated air was forced through each column for 2 weeks to promote pyrite oxidation in an attempt to regenerate acidity and high trace element levels. After oxidation, each column was leached with about 1 ℓ of deionized (Milli-Q) water and analyzed as above. Selected aliquots were analyzed for iron, aluminum, manganese, nickel, and arsenic. This subset of elements was selected as being indicative of general trace element behavior.

Complete results of this experiment are listed in Appendix B, Tables B-II through B-V. Results are shown in Figs. 13a and b. Concentrations of hydrogen, aluminum, nickel, fluoride, and arsenic were generally lower in the effluents from the three columns containing soil than in those of the control. In contrast, manganese concentrations were much higher and Fe(II) slightly higher in the soil-treated column leachates compared with those of the coal waste control. Treatment 1 is the least effective overall, at least during the initial leaching by the first liter of effluent water. However, none of the treatments alone produced an acceptable leachate during initial leaching by the first liter. Arsenic is the only contaminant satisfactorily controlled, but only by treatments 2 and 3.

After regeneration by oxidation with water-saturated air, effluent pH values of all four treatments decreased to low levels for the first few hundred milliliters. However the soil-treated columns exhibited more rapid pH increases than did the control. Iron concentrations were quite high after regeneration. Surprisingly, aluminum, manganese, nickel, and fluorine concentrations were higher in the effluents from soil-treated waste columns than from the control after oxidation. Arsenic was also higher, except in treatment 3. Except for manganese, these higher concentrations in soil-treated columns after regeneration are probably a result of acid leaching or dissolution of elements previously attenuated by ion exchange or precipitation at higher pH. In general, effluent trace element concentrations after air regeneration were quite high for all elements compared with initial effluent concentrations from the control, showing that considerable pyritic oxidation occurs with soil treated coal waste.

This experiment was designed to test the three soil treatments for effectiveness in reducing contaminant levels in the effluents from coal cleaning wastes. Treatment efficacy can be judged by three criteria:

(1) ability to reduce the high contaminant levels in the first few volumes of effluent to environmentally acceptable levels,
(2) ability to maintain steady-state concentrations at low levels, and
(3) ability to prevent oxidation of pyrite during post-burial air infiltration.

Regarding the first criterion, contaminant concentrations for all treatments are not reduced enough to use any of these as a primary control. In only one case (arsenic in treatment 3), was the initial effluent concentration sufficiently low.

These treatments also fail to meet the third criterion. That is, if air contacts the treated materials, appreciable pyritic oxidation occurs, resulting in the production of considerable additional soluble acidity and chemical elements.

Only the second criterion was met with some success. Steady-state concentrations of aluminum, arsenic, fluoride, and nickel are generally maintained at levels low enough to satisfy most environmental concerns. (Nickel and fluoride concentrations in treated columns are the same as those in the control.) Treated columns also maintain high effluent pH (> 6), compared with the control containing coal waste only. However, "steady-state" concentrations of manganese and ferrous iron are too high in all treated columns.

In the present experiments, treatments 1 and 2 used −3/8-in. soil mixed with the coal waste because this size would most likely be used in a practical application

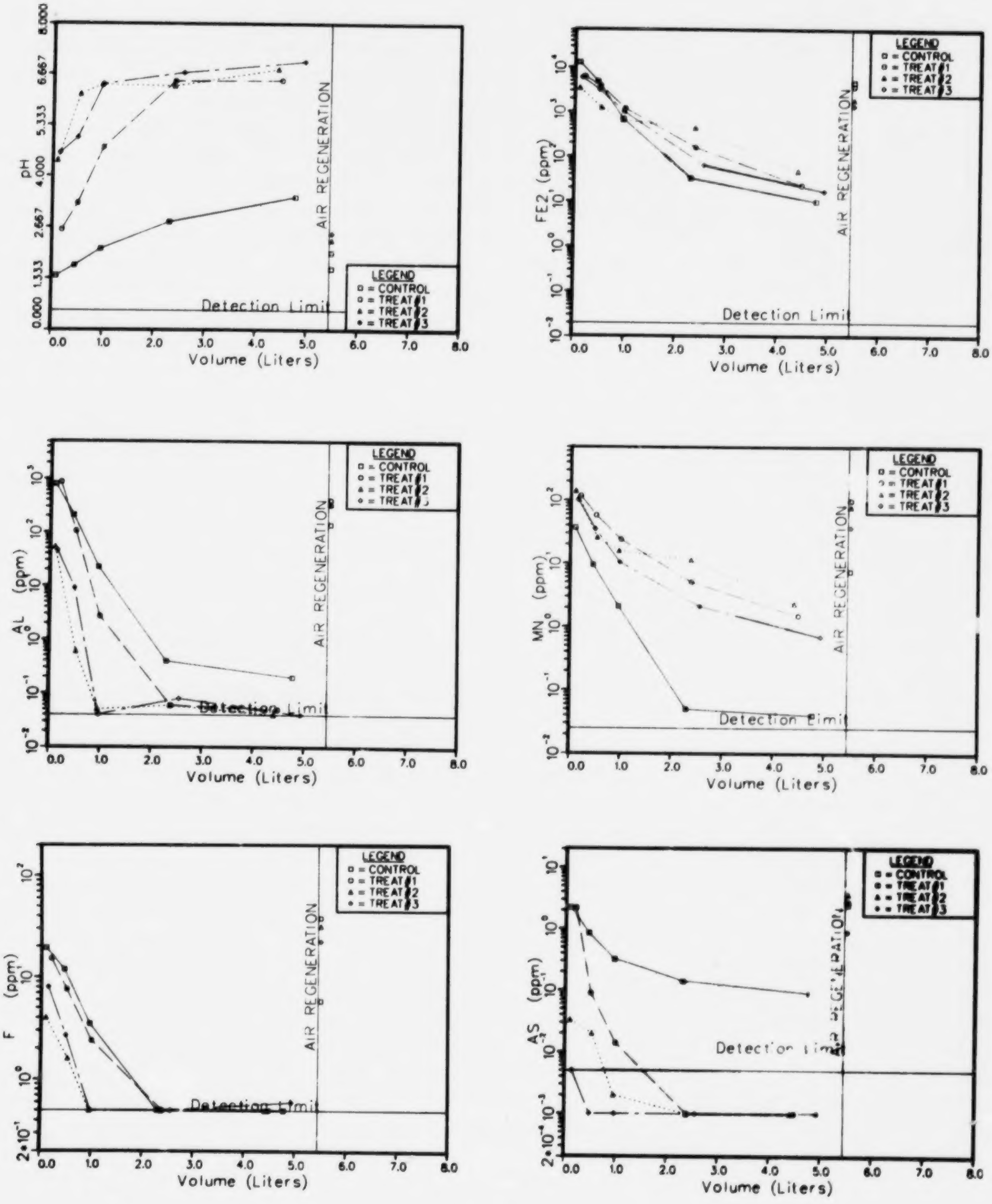

Fig. 13a.

Behaviors of pH, Fe(II), Al, Mn, F, and As vs effluent volume for the four treatments of Experiment A.

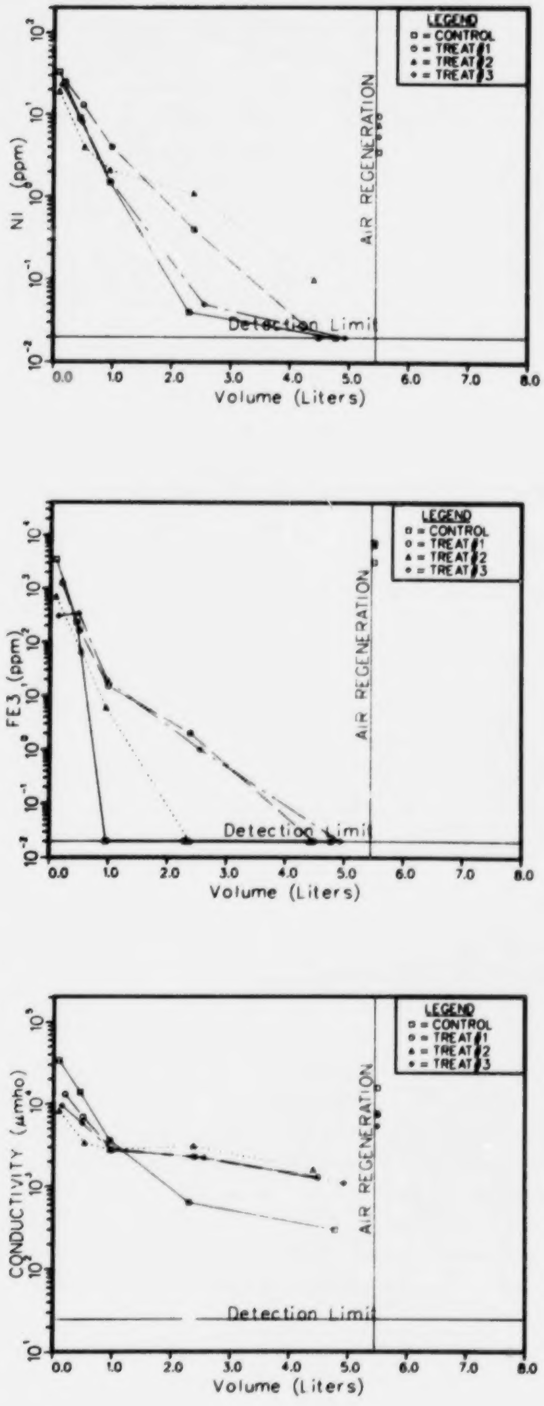

Fig. 13b.
Behaviors of Ni, Fe(III), and specific conductance vs effluent volume for the four treatments of Experiment A.

where overburden is codisposed with waste. However, we know that limestone, to be an effective treatment of acidity, should be ground to a small particle size because of the low solubility of limestone at high pH (> 6), and because limestone particles are deactivated by coating with sulfates and hydroxides formed as the coal refuse leachate is neutralized. Nevertheless, we hypothesized that, under water-saturated conditions, −3/8-in. soil might disperse, thereby providing ample surface area for neutralization.

Apparently the soil did not disperse and create enough additional available soil alkalinity to maintain a high pH during the production of initial leachate. However, there was sufficient alkalinity to eventually increase pH of the −3/8-in. soil-treated columns to a value above 6 after passage of 1.25 ℓ of leachate. This compares to a pH value of 2.1 for the control at a corresponding volume. The two columns capped with finely ground soil reached a pH of 6 after passage of only 0.5 ℓ. After removal of most Fe(II) and Al from the leachate, there was apparently adequate alkalinity available to produce a near-neutral leachate. It is possible that a slower leachate flow rate could provide more significant attenuation of hydrogen ion by this soil. Also, codisposal by mixing soil and waste might be more effective if the soil is finely ground. The next set of experiments addresses these possibilities.

These experimental results indicate that none of these soil-waste codisposal methods is adequate for controlling acidity and contaminant levels in leachates likely to be produced from water percolating through coal cleaning waste disposal piles.

b. Experiment B. Codisposal of Coal Cleaning Waste with Finely Ground Subsoils. This experiment was designed to test the effectiveness of codisposing soil and coal cleaning waste by mixing and burying them together. To ascertain whether such a procedure would be useful, finely ground soils (Table I) were completely mixed with −3/8-in. waste. Such mixing with finely ground soils is probably the optimum procedure possible but is probably unattainable in the field. However, we chose this procedure because a definitive answer to the technical feasibility of this control was desired. Also, if the results were unfavorable, no method practical in the field could be expected to be successful.

An amount of soil or overburden material having enough carbonate content to neutralize 150% of the coal waste acidity was mixed with the waste material in each column. One column (seam 11 overburden) was duplicated and left open to air to determine any difference in its behavior compared with columns maintained under argon (anoxic conditions).

About 4 ℓ of distilled water was passed through each column (upward flow) at a rate of 4-6 mℓ/h. Then the soil-waste mixtures were removed from the columns, allowed to air-oxidize for several days, and batch-leached using a 5:1 water-to-solid-mass ratio. Column influent, effluent, and batch leachates were monitored for pH, specific conductance, total iron, Fe(II), aluminum, arsenic, fluoride, manganese, and nickel. Ferric iron was determined by the difference between total iron and ferrous iron.

Raw results of this experiment are listed in Appendix B, Tables B-VI through B-XII. The results are summarized in Tables II-VIII and Figs. 14a and b. The behavior of eluent pH is discussed first because it is of principal importance to the chemistry of the other measured components. The pattern of eluent pH vs volume falls into the three patterns shown in Fig. 14a. The waste alone gives an initial eluent pH value of about 2.0, which slowly rises to about 2.5 after passage of 3 ℓ of water. (This quantity of water corresponds to an eightfold water-to-waste ratio). The eluent from the waste treated with acid soil varies from an initial pH of 3.7 to 3.5 after 3 ℓ of water is added. Thus, the acid soil does not raise leachate pH adequately and very little contaminant control is expected by the precipitation of solids. In contrast, alkaline soil treatment results in initial pH values between 4 and 5, rising fairly quickly to > 6 after passage of 1.4 ℓ of eluent. Thus, some control by alkaline neutralization would be expected for these calcareous materials.

General patterns of eluent concentrations for Al, Fe(II), Mn, F, Ni, and As are also illustrated in Figs. 14a and b for the control and for acid and alkaline soils. These patterns show that, for treated wastes, the concentrations of most of the measured species decrease rapidly with increasing eluent volume to values far below those of the control coal waste. Manganese is the major exception; it is apparently leached from the soil materials, themselves. These concentration decreases appear to coincide with pH behavior for the most part. These curves also show that air oxidation, after leaching, regenerates the low pH and high contaminant concentrations, once again pointing out the necessity for preventing air infiltration into abandoned coal waste dumps.

Quantitative aspects of these control experiments are discussed with reference to Tables II-VIII. In Tables III-VIII, we have listed the total amount of contaminant released per gram of coal waste in the first 3 ℓ of eluent,

TABLE II

EFFLUENT pH OBSERVED IN EXPERIMENT B DURING THE FIRST LITER OF ELUENT, AFTER ATTAINMENT OF NEAR STEADY STATE AND AFTER OXIDATION BY AIR

Sample	Soil: Waste Ratio	Initial[a] pH	Steady-State pH	After Oxidation pH
Control	–	1.9 – 2.4	2.7	2.3
Seam 11 (Argon)	0.67	4.2 – 6.4	7.9	3.0
Seam 11 (Air)	0.67	4.1 – 5.0	8.0	2.9
Seam 12	1.78	4.0 – 5.2	7.3	2.8
OKAW	5.38	3.6 – 3.9	3.3	3.0
BS 3	0.36	4.2 – 6.2	8.0	2.4
Quarry Limestone	0.087	3.8 – 5.4	8.0	6.4

[a] Initial pH over first liter of effluent.

TABLE III

SUMMARY OF *in situ* ATTENUATIONS OF ALUMINUM RESULTING FROM CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS AND A QUARRY LIMESTONE

Sample	Soil: Waste Ratio	Al Released[a]		Al Concentration (mg/ℓ)		
		Total (mg)	per gram of Waste	Av[b] Conc (mg/ℓ)	Steady State	After Oxidation
Control	–	360	0.99	120	~19	44
Seam 11 (Argon)	0.67	0.36	0.0010	0.12	<0.2	28
Seam 11 (Air)	0.67	1.32	0.0037	0.44	<0.2	34
Seam 12	1.78	24	0.113	8	<0.2	1.6
OKAW	5.38	23	0.242	7.7	2.5	11
BS3	0.36	0.10	0.0002	0.03	<0.2	84
Quarry Limestone	0.087	0.29	0.0005	0.10	<0.2	0.3

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[a] Milligrams of Al released into first 3 ℓ of eluent.

[b] Average concentration in first 3 ℓ.

TABLE IV

SUMMARY OF *in situ* ATTENUATIONS OF IRON (II) RESULTING FROM CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS AND A QUARRY LIMESTONE

Sample	Soil: Waste Ratio	Fe(II) Released[a]		Fe(II) Concentration (mg/ℓ)		
		Total (g)	per gram of Waste	Av[b] Conc (mg/ℓ)	Steady State	After Oxidation
Control	–	3.73	0.0100	1240	200	640
Seam 11 (Argon)	0.67	1.82	0.0050	607	<0.02	156
Seam 11 (Air)	0.67	1.70	0.0047	567	<0.02	198
Seam 12	1.78	2.40	0.0111	800	<0.02	152
OKAW	5.38	0.254	0.0027	85	30	36
BS3	0.36	1.68	0.0038	560	<0.02	566
Quarry Limestone	0.087	2.76	0.0050	920	<0.02	4

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[a] Grams of Fe(II) released into first 3 ℓ of eluent.

[b] Average concentration in first 3 ℓ.

TABLE V

SUMMARY OF *in situ* ATTENUATIONS OF MANGANESE RESULTING FROM CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS AND A QUARRY LIMESTONE

	Soil:	Mn Released[a]		Mn Concentration (mg/ℓ)		
Sample	Waste Ratio	Total (mg)	per gram of Waste	Av[b] Conc (mg/ℓ)	Steady State	After Oxidation
Control	–	7.4	0.020	2.5	0.6	1.4
Seam 11 (Argon)	0.67	40.4	0.112	13.5	0.8	28
Seam 11 (Air)	0.67	59.7	0.166	19.9	≤1	21
Seam 12	1.78	46.4	0.215	15.5	≤1	6.4
OKAW	5.38	104	1.11	34.7	20	31
BS3	0.36	149	0.339	49.7	≤2	11.3
Quarry Limestone	0.087	16.4	0.030	5.5	≤0.2	0.8

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[a] Milligrams of Mn released into first 3 ℓ of eluent.

[b] Average concentration in first 3 ℓ.

TABLE VI

SUMMARY OF *in situ* ATTENUATIONS OF FLUORINE RESULTING FROM CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS AND A QUARRY LIMESTONE

	Soil:	F Released[a]		F Concentration (mg/ℓ)		
Sample	Waste Ratio	Total (mg)	per gram of Waste	Av[b] Conc (mg/ℓ)	Steady State	After Oxidation
Control	–	7.75	0.021	2.6	0.4	0.68
Seam 11 (Argon)	0.67	~0.2	~0.0005	<0.2	<0.2	2.6
Seam 11 (Air)	0.67	~0.2	~0.0005	<0.2	<0.2	2.9
Seam 12	1.78	1.52	0.0071	0.5	<0.2	1.6
OKAW	5.38	1.48	0.016	0.5	~0.25	0.9
BS3	0.36	–[c]	–[c]	–[c]	<0.2	3.3
Quarry Limestone	0.087	–[c]	–[c]	–[c]	<0.2	<0.2

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[a] Milligrams of F released into first 3 ℓ of eluent.

[b] Average concentration in first 3 ℓ.

[c] All concentrations less than detection limits (0.2 mg/ℓ).

TABLE VII

SUMMARY OF *in situ* ATTENUATIONS OF NICKEL RESULTING FROM CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS AND A QUARRY LIMESTONE

Sample	Soil: Waste Ratio	Ni Released [a]		Ni Concentration (mg/ℓ)		
		Total (mg)	per gram of Waste	Av[b] Conc (mg/ℓ)	Steady State	After Oxidation
Control	–	7.41	0.020	2.5	0.5	1.1
Seam 11 (Argon)	0.67	6.68	0.018	2.2	<0.01	2.0
Seam 11 (Air)	0.67	6.32	0.017	2.1	<0.01	2.5
Seam 12	1.78	8.04	0.037	2.7	0.02	0.47
OKAW	5.38	2.13	0.023	0.7	0.2	0.51
BS3	0.36	2.41	0.005	0.8	<0.01	3.0
Quarry Limestone	0.087	4.45	0.008	1.5	<0.01	0.44

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[a] Milligrams of Ni released into first 3 ℓ of eluent.

[b] Average concentration in first 3 ℓ.

TABLE VIII

SUMMARY OF *in situ* ATTENUATIONS OF ARSENIC RESULTING FROM CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS AND A QUARY LIMESTONE

Sample	Soil: Waste Ratio	As Released [a]		As Concentration (mg/ℓ)		
		Total (mg)	per gram of Waste	Av[b] Conc (mg/ℓ)	Steady State	After Oxidation
Control	–	1.15	0.0032	0.38	0.08	0.14
Seam 11 (Argon)	0.67	0.0064	1.8E−5	0.0021	<0.001	0.004
Seam 11 (Air)	0.67	0.0051	1.4E−5	0.0017	<0.001	0.007
Seam 12	1.78	0.0110	5.1E−5	0.0037	<0.001	0.005
OKAW	5.38	0.0117	1.2E−4	0.0039	0.003	0.004
BS3	0.36	0.0021	4.8E−6	0.0007	<0.001	0.052
Quarry Limestone	0.087	8.0E−4	1.5E−6	2.7E−4	<0.001	0.001

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[a] Milligrams of As released into first 3 ℓ of eluent.

[b] Average concentration in first 3 ℓ.

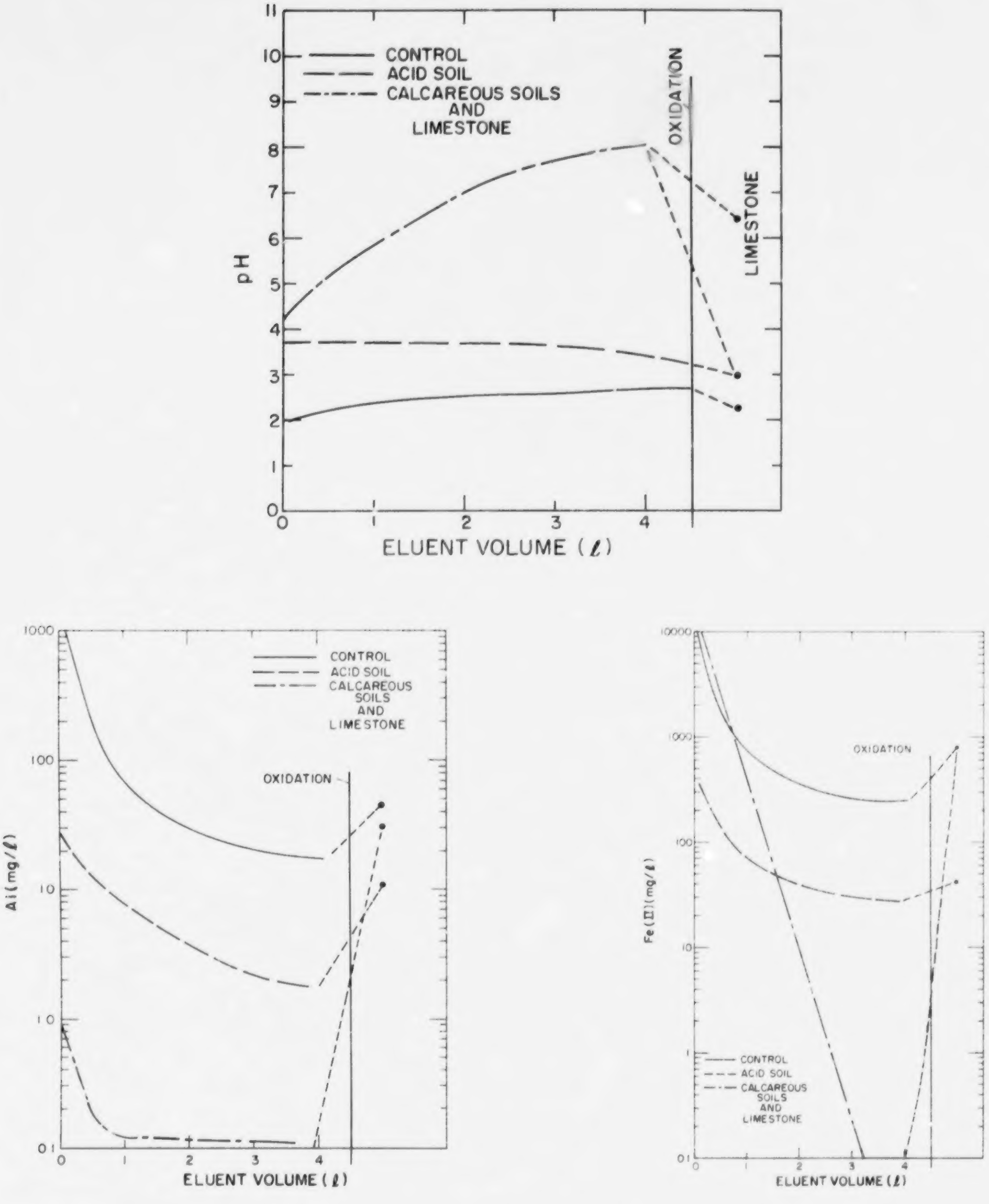

Fig. 14a.

General patterns of pH, Al, and Fe(II) in effluents from columns containing coal waste alone, coal waste plus an acidic soil, and coal waste plus calcareous soils.

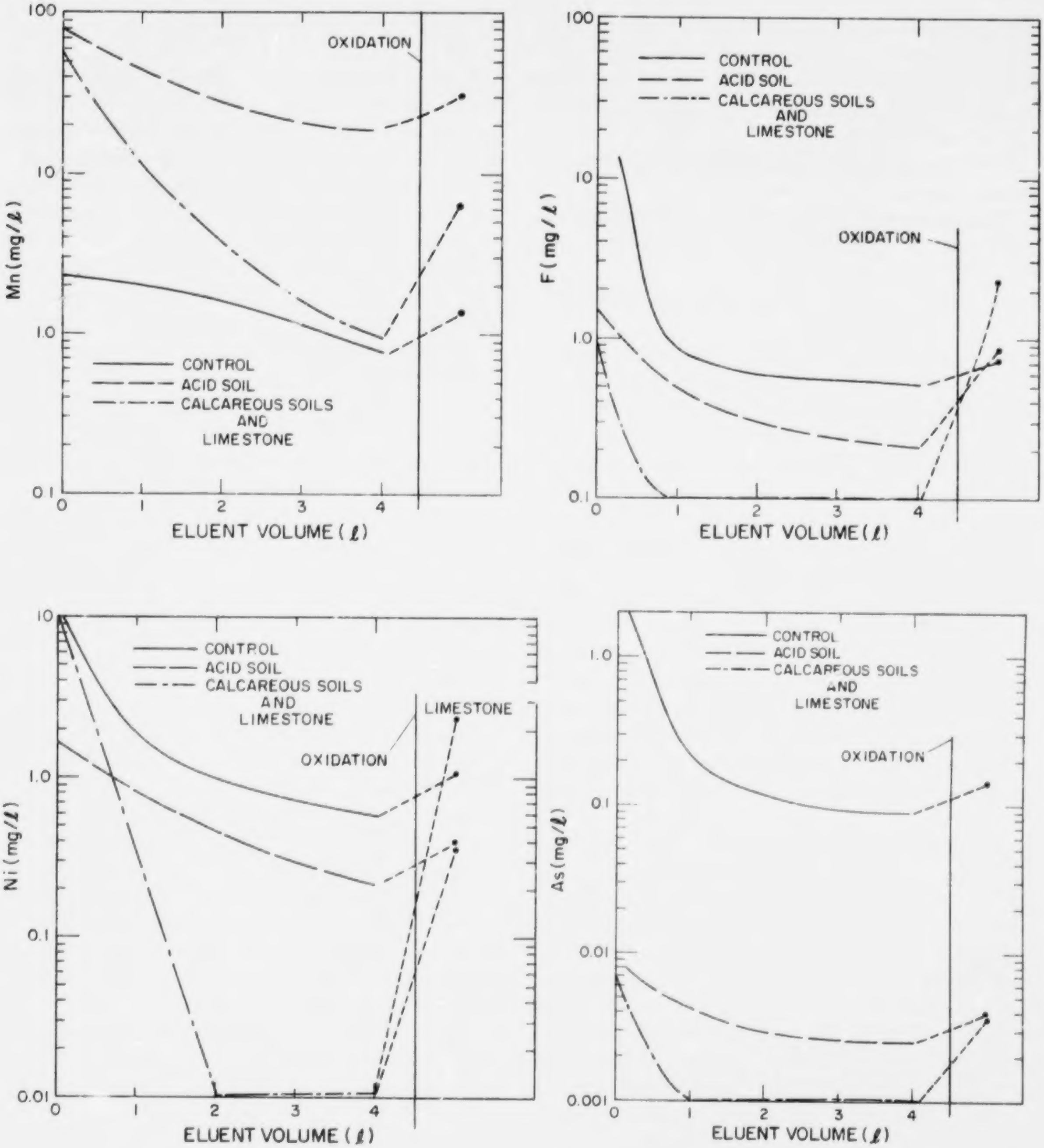

Fig. 14b.

General patterns of Mn, F, Ni, and As in effluents from columns containing coal waste alone, coal waste plus an acidic soil, and coal wastes plus calcareous soils.

the approximate concentrations at which a near steady state was attained after passage of several volumes of water, and the concentrations measured after oxidation by air. Each soil material should be compared with the control (no treatment).

Three criteria determine the efficacy of these environmental controls:

(1) control of initial large quantities of contaminant,
(2) control of steady-state concentrations at acceptable levels, and
(3) control subsequent to oxidation after leaching of initial contaminants.

Based on criterion (1), fluoride, aluminum, and arsenic are adequately controlled by some of the materials. The elements Fe(II), Mn, and Ni are not controlled and their concentrations remain unacceptably high. The pH values may not be acceptable depending on the water quality criteria used.

Steady-state concentrations are quite low in general, and thus, would be acceptable by most standards of water quality. The only exceptions are in the acidic OKAW soil where concentrations remain high for all contaminants except arsenic.

Trace element concentrations and pH after oxidation caused by allowing air to penetrate the soil-waste mixtures are, in general, not well controlled. Arsenic is an exception for several of the materials. Also the limestone treatment appears to be effective at maintaining lower concentrations and a high pH (6.4) after oxidation.

For each soil material, some codisposal mixture would probably maintain relatively low contaminant levels. However, to be practical in the field (using attainable ratios of soil to waste, mixing of materials, particle sizes reasonably obtained by conventional tillage procedures), we must conclude that codisposal of calcareous soil materials with the coal waste will not adequately control levels of several soluble chemical species present in coal waste. It will be necessary to provide a more readily soluble alkaline substance, such as $Ca(OH)_2$, than the carbonate minerals present in soils to control the large quantities of contaminant initially present in freshly disposed coal waste (or prevent their release by some other method). At present, our belief is that lime/limestone codisposal is a better control method than codisposal with soils.

B. Coal Waste Effluent Neutralization

Previous laboratory experiments in this program have shown the effectiveness of alkaline neutralization for limiting concentrations of inorganic chemical components in acidic leachates from coal cleaning wastes. Although it is generally assumed that these controls are caused by precipitation of insoluble carbonates, hydroxides, or other solids at the higher pH values attained, this assumption has not been investigated either experimentally or theoretically. As a result, we investigated the chemistry of a coal waste leachate system as a function of pH using MINEQL, a complex chemical equilibrium model designed for aqueous systems.[6] This study was made to test the applicability of chemical thermodynamic principles in understanding factors controlling the solubility of trace elements in a complex coal waste leachate. Results of the calculations were compared with the results of laboratory neutralizations of a waste leachate with $Ca(OH)_2$. In addition, the speciation of solution components and their controlling solids as predicted by the chemical equilibrium model were determined. Appendix C gives details on this investigation, including figures that compare empirical and theoretical (calculated) values. The most significant results of this work are summarized below.

Equilibrium concentrations were calculated using MINEQL for 24 chemical components, including the 11 elements identified as potential problems in coal waste leachates.[3] These were done at incremental pH values from 1 through 14 and for the specific pH obtained after the $Ca(OH)_2$ additions in the laboratory experiments. From these, total solution concentrations were calculated for comparison with experimental results. [After $Ca(OH)_2$ additions, chemical analyses were performed only for the 13 components listed in Table IX.] For thermodynamic predictions, multivalent species were assumed to be as follows; arsenic as AsO_4^{3-}, chromium as Cr(III), copper as Cu(II), and manganese as Mn(II). These assignments are consistent with a system controlled by the oxidation potential of an Fe(II)-Fe(III) couple. Because the experiments were performed under an argon atmosphere to prevent oxidation of Fe(II) to Fe(III), this reaction was not allowed in the thermodynamic calculations. The argon atmosphere also eliminated the need to consider $CO_2(g)$ exchange with our solutions.

TABLE IX

TOTAL SOLUTION CONCENTRATIONS OF THIRTEEN CHEMICAL COMPONENTS IN COAL WASTE LEACHATES AS MEASURED AFTER ADDITIONS OF CALCIUM HYDROXIDE AND AS PREDICTED BY A CHEMICAL EQUILIBRIUM MODEL

Lime Added (mmole)[b]	pH	Data Source	Final Element Concentration (mg/ℓ)[a]												
			Ca	Al	FeII	FeIII	AsO_4^{3-}	Cd	Co	Cr	Cu	F	Mn	Ni	Zn
0	2.25	meas.	350	370	1680	1630	0.76	0.21	3.5	0.43	0.09	81	9.9	7.5	16
		calc.	350	370	1680	1550	0.76	0.21	3.5	0.43	0.09	81	9.9	7.5	16
2.16	2.73	meas.	540	370	1800	160	0.26	0.23	3.7	0.28	0.11	86	10.1	7.7	17
		calc.	393	370	1680	70	0.76	0.21	3.5	0.43	0.09	81	9.9	7.5	16
4.75	5.82	meas.	430	0.46	1350	<0.02	<0.02	0.08	2.8	<0.01	0.01	2.0	10.8	3.8	3
		calc.	447	0.30	1260	0.002	0.76	0.21	3.5	0.43	0.09	4.0	9.9	7.5	16
5.8	6.49	meas.	450	<0.1	620	<0.02	<0.02	<0.03	0.5	<0.01	<0.01	4.2	8.1	0.5	0.5
		calc.	523	0.002	1200	0.0004	0.76	0.21	3.5	0.13	0.09	3.1	9.9	7.5	11.4
6.7	8.09	meas.	500	<0.1	2.2	<0.02	<0.02	<0.003	<0.02	<0.1	<0.01	10	0.3	<0.02	<0.02
		calc.	573	0.001	14.7	1.E-5	0.76	0.21	0.042	0.086	0.09	2.9	8.3	0.15	1.2
8.11	10.18	meas.	490	1.1	<0.02	<0.02	<0.02	<0.009	<0.02	<0.01	<0.01	12	<0.02	<0.02	<0.02
		calc.	664	0.17	5.01	0.0006	0.46	0.21	0.04	0.43	0.0003	2.6	0.30	0.0001	0.10

[a] Speciation used for equilibrium calculations: Ca, Cd, Co, Cu, Mn, Ni, and Zn divalent cations; Al, Cr as trivalent cations; F; AsO_4^{3-}.

[b] mmoles added to leachate (final volume 75 mℓ).

Comparisons of measured and predicted total soluble species concentrations after lime additions show good agreement for fluoride and the major cations Ca, Al, Fe(II), and Fe(III), but very poor agreement for trace elements As, Cd, Co, Cr, Cu, Mn, Ni, and Zn. These comparisons are shown in Table IX and illustrated for Fe(III), AsO_4^{-3}, and Zn(II) in Fig. 15.

Total solution concentrations of ferric iron (Fig. 15) were maintained at low levels by the precipitation of $Fe(OH)_3(s)$ in this system from pH 4-12. No significant solid forms of arsenate are predicted below a pH of 9 in this coal waste leachate. Laboratory measurements show arsenic concentrations to be lower than the detection limit of 0.01 mg/ℓ at pH 8.09 and 10.18. This is an approximate 500-fold discrepancy between measured and predicted concentrations (Fig. 15), indicating that some very important factor controlling AsO_4^{3-} chemistry in this system is not accounted for by the thermodynamic model. The comparison between measured and predicted concentrations for Zn(II) is intermediate between the extremes shown by Fe(III) and AsO_4^{3-}. Predicted zinc concentrations decrease from 16 mg/ℓ at pH 4.0 to a minimum of ~0.02 mg/ℓ at pH 9.0, followed by a rapid increase to 10 mg/ℓ at pH 12. Predicted zinc chemistry is almost completely controlled by the formation of soluble free cation and $ZnSO_4$ ion pairs below pH 7. By pH 7, nearly half the zinc is precipitated as the silicate, which, together with the insoluble hydroxide, limits soluble zinc to low concentrations between pH 7 and 10. Above pH 11, the formation of the negatively charged $Zn(OH)_3$ complex begins to return zinc to a soluble form in appreciable quantities. Measured zinc concentrations, after addition of $Ca(OH)_2$, begin to decrease at pH 5.82 and drop to values significantly lower than predicted (Fig. 15) between pH 6 and 10.

Similar to arsenic and zinc, measured concentrations of cadmium, cobalt, chromium, copper, manganese, and nickel are comparable to predicted concentrations at pH 2.73. In general, measured values of these elements begin to diverge to values lower than predicted at pH 5.82 and above. Of these, measured concentrations of nickel are substantially lower than predicted at pH 6.49, whereas measured values of manganese are substantially lower than predicted only at pH 8.09. Thus for all the trace elements except fluoride, measured concentrations fall below predictions, often by a considerable amount.

That the two major cations (aluminum and iron) are well accounted for in these calculations and that a charge

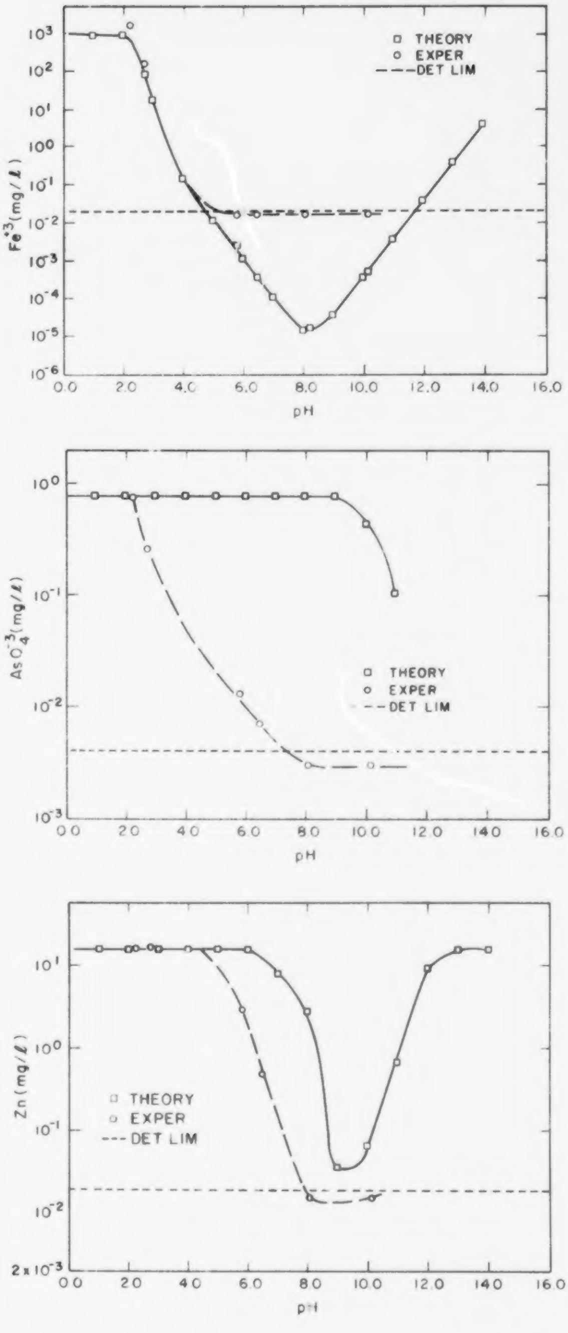

Fig. 15.
Concentrations of Fe(II), As, and Zn in coal waste leachates vs pH—comparisons of values predicted by thermodynamic calculations with those experimentally observed after additions of calcium hydroxide to coal waste leachates.

balance to within 10% is obtained suggests that all of the significant ligands have been included in the thermodynamic calculations. Consequently, we do not believe that some unknown solid phase can be invoked to account for the lower measured concentrations. The major cationic components (aluminum and iron) in these solutions form amorphous hydrous solid phases at all measured pH values. At pH > 5.5, virtually all of the Al and Fe(III) exist in the form of colloidal hydrous oxides. In addition, substantial quantities of other solid phases, $CaSO_4(s)$, $Fe(OH)_2(s)$, $FeCO_3(s)$, and $CaF_2(s)$, are present, which may very well serve as sorbing sites for trace elements. Several investigators[8-10] have shown that substantial quantities of various trace components are removed from solution by adsorption onto the surfaces of hydrous oxides; we postulate that such a mechanism is responsible for the discrepancy between experimental and predicted trace element concentrations in this work.

In general, chemical speciation is controlled by the major cations and anions and pH (Appendix C). The only anions present in substantial quantities are CO_3^{2-}, SO_4^{2-}, and F^-. At low pH, CO_3^{2-} is not present in an unprotonated form, thus, at pH 2.73, the only solid phases involve Fe(III) and Ca, which are present in high concentrations. Soluble cation species are dominated by free ions and sulfate or bisulfate complexes. At low pH, weakly acidic anions, CO_3^{2-}, SiO_3^{2-}, $B(OH)_4^-$, and AsO_3^{3-}, exist primarily as uncharged completely protonated species, whereas the strongly acidic anions are either complexed with Al, in the case of F^-, or precipitated as solids, in the case of PO_4^{3-}.

As pH increases, hydroxide and anions of weak acids become increasingly abundant, and therefore, important in solution chemistry. Solubility products of several carbonates and hydroxides involving both major and trace cations are exceeded. For example, at pH 6.49, Al has been removed from the solution by precipitation as $Al(OH)_3$, 70% of Cr exists as $Cr(OH)_3$, and 30% of Fe(II) is precipitated as the carbonate. Such trends continue as pH increases until most cations are maintained at relatively low concentrations at pH 8.09 because they precipitate as carbonates or hydroxides, or, in the case of zinc, as the silicate. At still higher pH (>10), many cations return to soluble forms as a result of the formation of negatively charged hydroxy species.

The anions of major interest (SO_4^{2-}, F^-, $B(OH)_4^-$, AsO_4^{3-}) are not well controlled by precipitation as solid phases except for F^-. Predicted concentrations of F^- are maintained below 4 mg/ℓ at pH ≥ 5.82. No solid phases of AsO_4^{3-} are indicated before the formation of $Ca_3(AsO_4)_2$ (s) at pH > 10. Solid phases involving boron are nonexistent according to the calculations. A considerable amount of $CaSO_4(s)$ is predicted at all pH values between 2.73 and 10.18, but because of its large abundance (12 000 mg/ℓ in the initial leachate), SO_4^{2-} concentrations remain high at all pH.

In summary, these results show that application of chemical thermodynamic principles to problems in environmental control can assist in the understanding of factors controlling the solubility of potential contaminants. Alkaline neutralization is even more effective than anticipated, based on solubility controls alone. We believe this to be due to adsorption of trace components onto the surfaces of solids formed as the pH increases. Adsorption itself is a sensitive function of pH and might be maximized by proper selection of final pH.

C. Calcination of Coal Wastes

In previous reports, we demonstrated that calcination can convert high-sulfur coal wastes to innocuous forms[2-4] because, at high temperatures (600-1000°C), the sulfur is driven off in the form of SO_2, and thus the acid-generating potential of the waste is drastically reduced.[4] In addition to sulfur, however, other volatile elements (bromine, cadmium, and lead) are driven off in appreciable quantities. Consequently, the calcining of coal wastes is a conversion process in which the problem of acid drainage is alleviated while incurring an air pollution problem caused by SO_2 and volatile trace elements. We reported some attempts at controlling the sulfur emissions in such a process, but the cost of these controls will be high, regardless of the method used.

In the past year, we completed calcination studies of coal wastes from Plant K. Plant K, in Pennsylvania, processes high-sulfur Appalachian coal. In Sec. II.B we show that this waste is mineralogically quite similar to high-sulfur coal wastes from the Illinois Basin. The calcining behaviors of these wastes, however, appear to be somewhat different as shown by the data in Table X.

Table X shows the trace element leachabilities for calcined coal wastes from Plant K, along with those for the same wastes combined with selected chemical additives before calcination. Previously reported values for Plant B are also included for comparison.[3] These calcinations were all done at 1000°C for 2 h. Although this treatment does dramatically reduce the trace element leachabilities of Plant K refuse, it is evident that the calcined refuse from Plant K is considerably more

TABLE X

TRACE ELEMENT LEACHABILITIES OF CALCINED COAL PREPARATION WASTES WITH AND WITHOUT SELECTED CHEMICAL ADDITIVES

Refuse Type	Plant K (Appalachian Region)					Plant B (Illinois Basin)
Additive	–	$CaCO_3$	$CaCO_3$	KNO_3	KNO_3	–
	–	5 wt%	10 wt%	5 wt%	10 wt%	–
Element						
Al	38.5	<0.6	<0.6	122	397	0.4
Mn	34.1	<0.03	<0.03	34.1	56.4	0.03
Fe	5.7	<0.3	0.31	17.1	267	<0.03
Co	0.57	<0.03	<0.03	1.17	1.83	<0.01
Cu	1.37	0.17	0.17	0.36	0.50	0.01
Ni	0.87	<0.03	<0.03	1.19	2.5	0.01
Zn	0.67	0.08	0.16	4.53	7.28	0.05
Cd	<8	<0.003	<0.003	0.003[b]	0.003[b]	<0.001
pH	3.9	11.51	11.33	4.05	4.00	8.0
TDS, wt%[c]	0.21	0.40	0.52	0.70	1.60	0.2

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[a] Concentrations are in μg/cm³ in the leachates.

[b] ±0.003.

[c] TDS = total dissolved solids.

leachable than other calcined wastes that we have previously studied. This is surprising in view of the similar mineral compositions of these materials.

We carried out several experiments in which chemicals were added to the refuse before calcining, hoping to accelerate the sintering and oxidation of the various mineral phases. The results of these experiments are also shown in Table X. Addition of limestone ($CaCO_3$) elevates the pH and reduces the trace element concentrations of the leachates; however, it is not apparent from this experiment that addition of calcium carbonate followed by calcining is any different than simple addition of calcium oxide to the refuse. Nitrate salts might be expected to promote the oxidation of sulfur-containing minerals, but such behavior was not observed in this experiment. In fact, many of the trace elements show much increased leachability in the presence of nitrates.

Table XI contains the same data as Table X, but they are expressed in terms of discharge severities. These were determined by finding the ratios of the elemental concentration to 100 times the ecology MATE values for the corresponding elements. In certain respects, the discharge severities are more useful than the elemental concentrations because they reveal the extent to which each element in the leachate might threaten the environment. Table XI shows that calcined waste from Plant K still has appreciable discharge severities for manganese, nickel, and, to a lesser extent, aluminum, copper, and iron. Under these conditions, calcination of Plant K wastes does not produce an entirely innocuous waste.

It is not clear why the wastes from Plant K behave differently than those previously studied. We believe that calcination conditions can be devised to control these materials. However, the cost of the calcination process is

TABLE XI

DISCHARGE SEVERITIES FOR THE LEACHATES FROM CALCINED COAL PREPARATION WASTES

Refuse Type	Plant K (Appalachian Region)					Plant B (Illinois Basin)
Additive	–	$CaCO_3$	$CaCO_3$	KNO_3	KNO_3	–
	–	5 wt%	10 wt%	5 wt%	10 wt%	–
Element						
Al	0.38	<0.006	<0.006	12.2	40	0.004
Mn	3.4	<0.003	<0.003	3.41	5.6	0.003
Fe	0.23	0.012	0.012	0.68	11	<0.001
Co	0.023	<0.001	<0.001	0.047	0.073	<0.0004
Cu	0.27	0.034	0.034	0.072	0.10	0.002
Ni	0.87	<0.03	<0.03	1.2	2.5	0.01
Zn	0.067	0.008	0.016	0.45	0.73	0.005
Cd	<80	<0.03	<0.03	0.03	0.03	<0.01
pH	3.9	11.5	11.3	4.0	4.0	8.0

[a] Discharge Severity = (Concentration)(0.01) ÷ (Ecology MATE).

so high that it may never be used on any commercial scale.[3,11] Thus, though pyrolysis of coal wastes is important to our research in control technology and to our understanding of the behavior of the mineralized coal wastes, it does not have a high priority in our research program at this time.

D. Summary and Conclusions

During the past year, we have addressed four types of environmental control strategies. These include disposal of the waste after treatment with lime and limestone, codisposal of the waste with alkaline soils or other process wastes, neutralization of the coal waste effluents, and calcination of coal wastes, with and without chemical additives. The most effective of these treatments is the lime/limestone treatment.

Coal waste that has been sequentially slurry-coated with lime and then limestone results in leachates of acceptable environmental quality for periods of at least 4 months. This treatment is not permanent, but it is cost effective and may be useful as part of a more comprehensive strategy that will provide for ultimate disposal of the treated coal wastes under anaerobic conditions. At present, several unanswered questions remain. The most important is whether results of our studies with one coal waste are representative of all coal wastes, or at least coal wastes of certain mineral compositions. We must also determine the optimum treatment conditions. Furthermore, several environmental factors, such as freeze-thaw cycles, compaction of the waste pile, and permeability of the waste pile, must be evaluated. Finally, the mechanism by which this process works needs to be understood so that its limitations can be determined and improvements made. In spite of these issues, the lime/limestone treatment is the most promising control strategy investigated so far, and we will continue intensive studies during the coming year.

Alkaline soils or process wastes, mixed directly with the coal waste or placed in series with the effluent flow, is partly effective in controlling trace element releases from the waste pile. However, none of the materials tried gave an entirely acceptable leachate. The main difficulties arose after air regeneration of the acid within the waste. The high initial acid contents of the resulting leachate overwhelmed the capacity of the soils or process wastes to deal with it, although the treated wastes recovered more quickly than those which were not treated. In addition, because many of the materials mixed with the waste contained leachable forms of manganese and iron, they were ineffective in controlling these elements. Nevertheless, the information obtained from these experiments is very useful in assessing potential effects of the mineralogy and structure of hypothetical waste disposal sites. For example, this information can suggest the optimum structure of a waste disposal site in terms of the underlying soil layers and location of the site. Future emphasis in this area will be on determining the effects of natural soils and mine overburdens on the effluents of coal waste piles.

Neutralization of acid mine drainages and coal waste effluents is the most widely practiced environmental control for these types of problems because of its simplicity and low cost. For this reason and also because acid neutralization is the basis of our most effective control efforts, we have investigated this process and its limitations. Comparisons of experimental results with those from thermodynamic calculations reveal that the major cation concentrations are controlled by solution-precipitation chemistry, which is reasonably well understood. However, the trace element concentrations are significantly lower than theory predicts. As expected, the speciations of most of the elements is controlled by the major ions in solution, but the anion behavior is not well accounted for except for fluoride. We believe that the low trace element concentrations are caused by adsorption of ions on the highly dispersed colloidal precipitate formed during the neutralization process. Understanding these phenomena would allow us to extrapolate our experimental results to other systems and would add to our predictive powers.

Calcining coal wastes reduces the starting material to an innocuous form, but this exchanges one problem for another because large amounts of sulfur and trace elements must be removed from the gaseous by-products. Coal wastes from Plant K behave differently than those studied before. Specifically, calcined waste from Plant K still yields leachates containing environmentally significant amounts of manganese and nickel, and, to a lesser degree, aluminum, copper, and iron. We believe successful calcining conditions could be found to reduce waste from Plant K to innocuous form, but previous cost studies show that this approach is costly in comparison with other methods. Consequently, we will not study this technique further at this time.

II. ASSESSMENT OF HIGH-SULFUR APPALACHIAN COAL WASTES

A. Introduction

Our early studies were with high-sulfur coal wastes from the Illinois Basin, and most of our reported work has dealt with these materials.[1-3] Last year, we reported assessments on low-sulfur Appalachian coal wastes (Plant G).[4] We are now investigating high-sulfur coal wastes from Appalachia (Plants I and K) and have obtained some pertinent information on these wastes.

Some of the particulars regarding Plants I and K are summarized in Appendix D. Both plants are in western Pennsylvania and process coal from the Kittanning and Freeport seams. Plant I uses cyclones to clean the coal. All incoming coal is reduced to −3/4 in. with a rotary breaker so that the refuse consists of −3/4-in. waste and the breaker reject. We have completed most of the experimental work, but the data are incomplete and have not been reduced to a usable form. Results for Plant I will appear in our next annual progress report. Plant K is a jig operation in which only the coarse coal (+3/8 in.) is cleaned. The fine coal goes directly through the plant and is combined with the cleaned coal. Waste streams consist of coarse refuse and a slurry containing -60-mesh fines. In the present assessment, we consider only the coarse waste. The results for Plant K are mostly complete. The only missing data are the atomic absorption analyses for the solid starting materials. Available results from neutron activation and emission spectroscopy are reported here; complete assessments on both plants will be included in our next annual report.

B. Mineralogical Analyses

Coal waste samples were dried at 60°C. Each of four barrels was sorted separately into fractions according to gross mineralogical appearance. All the −1/2-in. material was first screened out. This unsorted ($\leq$1/2-in.) material constitutes sample 52G. The larger pieces were sorted in piles according to appearance. Because fine coal dust covered most of the material, properties such as apparent density also had to be accounted for. Luster, color, and form were all factors in the sorting. No quantification of hardness or density was attempted. In a few cases, rocks were broken to reveal their features more clearly, and all the fragments were placed in the same appropriate piles. The numbers and types of piles were not predetermined; a pile was formed as a significant number of similar rocks were placed together.

The material from Plant K naturally divided into seven fractions that can be characterized as follows:

Sample 52B (13.9%) looks like coal, with block cleavage, but has a resinous rather than a vitreous luster. In general, the pieces were cubic with 1- to 2-in. sides.

Sample 52C (27.6%) contained pieces, some quite large (2 to 6 in.), that had black, vitreous, coaly material adhering to whitish or dull metallic pyrite. The weight of these pieces compared to similarly sized coal or clay was a distinguishing feature.

Sample 52D (25.3%) contained pieces, generally less than 2 in. across, of roundish, whitish clay, that often broke into layers. The pieces were typically coated with a yellowish, powdery substance.

Sample 52E (4.0%) pieces were dark, hard, heavy, and coated with a thin layer of rust-colored substance.

Sample 52F (5.8%) labeled "miscellaneous +1," consisted mainly of large slabs of shale-like material, typically ~1/2 in. thick.

Sample 52G (20.2%) was a collection of all the original material that passed through a 1/2-in. screen.

Sample 52H (3.2%) was material that could not be classified into any of the above fractions. The sample included chunks of orange-colored sandstone, small clay balls with unidentified inclusions, and a few pieces of granite, a material not known to be indigenous to coal deposits.

We also generated a composite sample, 52A, by recombining representative samples split from each of the seven fractions described above.

These fractions, as well as the composite waste material, a feed coal, and a clean coal from the same plant were plasma-ashed at 150°C. The resultant low-temperature ash was ground to -200 mesh in a mechanical mortar and pestle. A portion of each was mixed with 1 μm alumina powder as an internal standard (to approximately 20 wt% alumina). A lightly compacted sample was then examined by x-ray diffraction. Relative peak heights of the major minerals were determined by direct measurements of the diffraction tracings. The quantitative mineral composition was obtained by means of a computer program that converts the raw digitized peak-height data to percent mineral present, using predetermined standard calibration curves for the minerals in the program library.[2,12,13] Results of the analyses of mineral content are shown in Table XII. Because of uncertainties in the measurement of the diffraction intensities and the many assumptions involved in deriving the quantitative values, errors for the major mineral components may be ~20%, and those for the minor components could be larger.

Unlike the Illinois Basin wastes previously examined, this waste has little or no marcasite. However, the pyrite content in composite sample 52A, is comparable to that in the high-sulfur Illinois Basin coal wastes that we have studied. The fractions containing clays also contain relatively large amounts of illite compared with the Illinois Basin waste; however, the illite content (16%) of composite sample 52A is comparable to that in the composite samples for both Plant G (low-sulfur Appalachian) material (19%) and Illinois Basin waste from Plants A (14%) and C (16%). Kaolinite varies from 10 to 16% throughout the samples of average waste analyzed from both the Illinois Basin and Appalachian region, except for Plant B, with 7% kaolinite in the average waste samples. Mixed-layer clays of statistically significant amounts were found only in fraction 52B and in the cleaned coal of the Plant K samples. Montmorillonite was not positively identified in any sample. The quartz content seems to vary little in the average samples from plant to plant, but was highly concentrated in fraction 52H, a piece of granite-like rock of unknown origin. Quartz is also concentrated in fraction 52D, a clay fraction.

One component of the Plant K waste, not observed in any other coal preparation waste that we have studied, is siderite ($FeCO_3$). It could not be quantified by our computer program, but we estimate it to be present in the greatest concentrations in fraction 52E (rusty material), in moderate concentrations in fraction 52B (smooth, block cleavage fraction), in lesser amounts in fraction 52A (composite waste) and 52G [miscellaneous -25-mm (~1-in.) fraction], decreasing in fractions 52F, 52H, and 52D, and absent in fraction 52C (pyrite with adhering coal fraction). Small amounts are also present in both the feed and cleaned coal samples. The type of siderite identified might have 1-2% manganese in its structure, as an iron replacement in the crystal.

Another component of the material could not be identified as belonging to any major mineral group mentioned, which may indicate the presence of amorphous noncrystalline matter undetectable by x-ray diffraction analyses. (This and the siderite compose the quantity labeled "unknown" in Table XII.)

The mineralogical information reported here will be used to determine the trace element and mineral associations in the plant K coal waste. In turn, that information may be used to develop models to aid our understanding

TABLE XII

MINERALOGICAL COMPOSITIONS OF COAL WASTES SAMPLES FROM PLANT K

	52A[a]	52B	52C	52D	52E	52F	52G	52H	53	54
Pyrite	25	8	53	4	23	13	23	2	6	2
Marcasite	Trace	Trace	0	0	Trace	0	0	0	Trace	0
Quartz	19	15	5	28	16	16	16	(51)[b]	7	5
Calcite	0	0	0	0	0	0	0	0	0	0
Gypsum	1	Trace	0	Trace	2	1	1	1	Trace	0
Illite	16	6	3	29	15	19	12	28	7	4
Kaolinite	10	9	3	15	7	12	8	15	7	6
Montmorillonite	0	0	0	0	0	0	0	0	0	0
Mixed Clay	0	9	Trace	0	0	Trace	0	0	0	3
Unknown	7	15	4	17	24	19	16	0	4	8
LTA	76.4	62.2	68.7	92.5	86.8	79.6	76.2	97.0	31.1	28.0

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[a] 52A: Composite waste sample.
52B: Smooth, block cleavage fraction.
52C: Pyrite with adhering coal fraction.
52D: Whitish, roundish clay fraction.
52E: Black fraction having rust-colored coating.
52F: Miscellaneous +25 mm (+1 in.) fraction.
52G: Miscellaneous −25 mm (−1 in.) fraction.
52H: Fraction largely consisting of granite, sandstone, etc.
53: Average feed coal +9.5 mm (+3/8 in.).
54: Average cleaned coal +9.5 mm (+3/8 in.).

[b] The quartz value was too high to be calculated directly; the 51% was obtained by difference.

of trace element mobilities and leaching behaviors of coals and their mineral wastes.

C. Chemical Composition

Elemental analyses were performed on each fraction. Lithium, beryllium, silicon, silver, cadmium, sodium, and calcium were determined by optical emission spectroscopy and the remaining elements were measured by neutron activation analysis. The one exception is sulfur, which was determined by chemical means. The results of these analyses are displayed in Table XIII. This table shows that, in general, these samples have low calcium contents, consistent with the mineralogical observation that little or no calcite is present. In general, the samples have slightly less sulfur than appears in similar samples from the Illinois Basin. The levels of lithium, chlorine, arsenic, cadmium, antimony, and lutetium are higher than in samples from the Illinois Basin. Among these, arsenic, antimony, and cadmium may be significant if they are mobilized in the waste leachates. In general, zinc and rubidium levels are lower than those observed in other high-sulfur coal wastes.

Because the sample fractions are substantially different mineralogically, we can derive some information about the tendencies of various trace elements to associate with certain minerals. Silicon is predictably highest in those fractions containing the most quartz and clays, and lowest in the fractions containing large amounts of pyrite. Sodium, magnesium, aluminum, and potassium show the same trends. Calcium is uniformly smeared through all the fractions. Sulfur is markedly more concentrated in the phases with the most pyrite,

TABLE XIII

ELEMENTAL COMPOSITIONS OF COAL WASTE SAMPLES FROM PLANT K (DRY BASIS)

Sample	52A	52B	52C	52D	52E	52F	52G	52H	53	54
	Composite Waste	Coal Waste Fractions							Feed Coal	Cleaned Coal
Li	100	92	18	69	42	52	89	54	23	19
Be	<1	<1	<1	2.3	<1	0.8	<1	1.4	2.0	2.4
B										
F										
Na(%)	0.28	0.27	0.04	0.30	0.26	0.55	0.39	0.36	0.08	0.09
Mg(%)	0.51	0.34	0.08	0.86	0.58	0.68	0.52	0.66	0.18	0.07
Al(%)	6.2	5.6	1.7	12.2	4.0	8.8	6.4	6.1	3.3	2.5
Si(%)	14	14	5.1	30	14	20	19	>37	6.1	6.1
P										
S(%)	9.74	4.40	23.6	1.30	10.75	4.04	11.46	0.58	2.9	1.64
Cl	250	195	320	76	<100	140	210	<20	990	1030
K(%)	1.0	1.1	0.22	2.8	0.76	1.8	1.2	1.6	0.50	0.32
Ca(%)	0.34	0.31	0.23	0.27	0.47	0.19	0.24	0.47	0.21	0.19
Sc	11.8	12.1	3.0	22	8.4	16.8	10.5	9.9	7.7	6.1
Ti(%)	0.49	0.45	0.17	0.84	<0.10	0.58	0.41	0.55	0.21	0.17
V	75	69	28	130	38	113	79	74	48	41
Cr	77	62	20	127	37	78	56	54	49	28
Mn	300	720	43	103	1360	183	270	250	74	54
Fe(%)	13.7	7.4	30	3.0	24	7.2	12.4	4.0	3.3	1.6
Co	16.6	14.3	14.3	16.9	21.0	18.3	16.9	8.9	11.7	9.6
Ni										
Cu	<100	<200	<70	<100	<400	<100	<100	<100	<100	<100
Zn	11.7	118	<4	<3	<50	97	71	71	<100	102
Ga	<20	<10	<30	33	<20	21	<20	12	<10	<10
Ge										
As	320	123	800	28	196	115	280	24	114	26
Se	10.9	10.9	13.8	2.3	27	7.4	11.7	5.4	<3	4.8
Br	17	22	19	4.3	7.8	12	18	3.3	54	50
Rb	<70	<50	<60	177	<80	147	118	87	<40	<30
Mo										
Ag	<0.8	<0.7	<0.8	<0.9	<0.9	<0.8	<0.8	<1.0	<0.5	<0.5
Cd	21	10	39	14	15	9	20	<8	8	<8
Sn										
Sb	5.2	3.3	19.9	2.3	3.5	4.3	9.7	1.2	3.4	1.7
I	<10	<20	<6	<9	<40	<10	<10	<10	18	17
Sr	<200	<300	100	500	<500	<200	<200	<200	<100	240
Cs	4.6	3.8	<0.8	8.3	2.8	7.2	4.1	2.6	2.1	1.5
Ba	330	330	92	540	<200	380	340	270	200	130
La	40	34	17	65	22	50	50	34	22	15
Ce	78	62	29	144	48	103	71	69	46	32
Sm	<0.06	12.8	5.9	13.2	10.5	5.6	21.0	5.7	10.3	6.5
Eu	0.9	0.8	0.4	1.5	0.8	1.4	0.9	0.8	0.6	0.5
Tb	<2	<2	<0.9	2.1	<2	1.8	1.8	1.2	1.6	<0.8
Dy	4.7	6.6	2.1	7.9	<1	7.1	5.2	5.3	4.2	3.3
Yb										
Lu	1.2	1.2	<0.2	1.9	<0.4	0.6	<0.2	1.0	1.0	<0.2
Hf	4.9	4.6	1.2	7.5	3.0	5.2	3.6	9.0	2.2	1.2
Ta	<0.7	<0.6	<0.6	1.1	<0.7	<0.5	<0.4	0.8	<0.6	<0.4
W	1.1	3.9	<1	1.6	<0.007	<1	3.3	3.6	<0.01	<0.6
Hg	0.07	<0.02	0.07	<0.02	0.10	0.03	0.04	<0.01	<0.02	<0.01
Pb										
Th	13.3	11.1	3.1	21.1	7.3	14.4	9.8	10.0	7.5	4.8
U	3.1	3.3	1.1	5.2	1.7	4.4	3.0	3.3	2.1	1.8

which agrees with our perception that pyrite is the major sulfur-bearing component in the coal waste. Iron is most concentrated in the fractions with the most pyrite, but it is also abundant in the fractions with large unknown components and in certain clay fractions. This suggests that the unknown component may contain microcrystalline pyrite, but it may also indicate that some of the clays contain significant amounts of iron. Titanium seems most concentrated in the phases with the most quartz and clays and least concentrated in the high-pyrite phases. Thus, the titanium is probably present as the oxide, either in a discrete mineral phase, or as a component of the quartz or some of the clays.

The alkali metals and alkali earths tend to concentrate in the fractions with the highest clay contents and in those with the highest quartz values; the lowest amounts are found in the fraction that is mostly pyrite. These findings agree with our understanding of the chemistries of these elements, since we expect these elements to be associated with various aluminosilicates. In group VIIA (halogens), we have experimental data on only chlorine and bromine. Similarly, in group VIA, we have data only for sulfur and selenium, and in VA, we have data for arsenic and antimony. However, these elements all show the same trends. They tend to be most concentrated in the pyrite phases and least concentrated in the quartz phases. Some of these (selenium, arsenic, and antimony) may have serious environmental implications. In group IVA, we have data only for silicon, and in group IIIA, our information is restricted to aluminum, which is predictably associated with the clays.

Among the transition metals, most are associated with clay-bearing fractions and are least concentrated in the pyrite-containing fractions. These include titanium, scandium, vanadium, chromium, thorium, and uranium. Manganese seems to be somewhat different because it tends to associate with the fractions containing large unknown components and may be associated with the iron there. Manganese is least concentrated in the pyrite fractions. It is hard to draw conclusions about cobalt, except that it is least abundant in the pyrite fractions. The same is true for zinc. Cadmium is notably different because it tends to associate with the high-pyrite fractions and presumably is present as the sulfide. The rare earth elements that we have determined, with the possible exception of samarium, are associated with the fractions having high contents of clays and other silicates, and are least evident in the fractions with the most pyrite. Notably absent from this analysis are mercury and lead. The lead analyses are not available yet, and the data for mercury [illegible] of insufficient quality to draw conclusions. We expect both elements to be associated with the sulfide (pyrite) phases.

In general, the materials from Plant K are comparable to those from the Illinois Basin. The sulfur levels are slightly lower, and the concentrations of a few of the trace elements are higher in the Plant K materials (lithium, chlorine, arsenic, cadmium, antimony, and lutetium) and others are slightly lower (zinc and rubidium). The Plant K waste has little or no calcite and, hence, should have correspondingly little self-neutralizing capacity. Trace metals likely to cause concern because of water quality tend to be associated with the clays and silicates in the samples. However, several important elements (selenium, arsenic, antimony, cadmium, iron, and possibly others) are associated with the sulfide phases (pyrite). In our samples, the trace element and mineral associations essentially agree with our understanding of the chemistries of these elements.

D. Micromineralogy

To determine the structural relationships of trace elements and minerals, fractions of waste (sorted according to gross mineral appearance) and feed and cleaned coals from Plant K were examined by a scanning electron microscope (SEM) equipped with an energy dispersive spectrometer (EDS). Procedures for sample preparation, techniques for distinguishing mineral forms, and photomicrographs of typical coal/coal waste mineral forms have been published in Ref. 14. Microscopic examination of bulk mineralogical samples is subject to severe sampling errors because so little of the sample is studied at any one time. The situation is analogous to the fable of the six blind men and the elephant. In this story, each of the blind men, after examining only a small part of the beast, draws completely erroneous conclusions about the nature of the animal. Only by pooling their knowledge can the six observers reach the correct conclusions. Similarly, with our coal waste samples, a very large number of random microscopic examinations must be made to complete a representative analysis of the bulk sample. Unfortunately, microscopists tend to concentrate on those particles that are either easily observed (high atomic number) or that are particularly interesting (unique). Since neither of these particle types is likely to be representative of the sample as a whole, one can be easily misled by these observations. In spite of these limitations, the SEM/EDS combination can perform elemental analysis while retaining spatial resolution. This allows conclusions to be drawn about the elemental associations within the sample—very difficult to do by other means except in indirect ways.

Certain assumptions must be made in order to derive the mineral composition of the particles observed by the scanning electron microscope. Because SEM/EDS analyses cannot detect elements below sodium in atomic number, many references to mineral types reported here are conjecture, based on their known presence as determined by x-ray diffraction analysis for major minerals, or, as in the case of microminerals, on the probability of the existence of a particular element in that form. For example, if titanium is detected alone, it is probably as TiO_2, but whether it is of the anatase or rutile or other crystallographic form cannot be determined.

Although a few trace elements may be chemical constituents of a major mineral phase, such as calcium in calcite or gypsum, they usually are found in what appears to be a physical, rather than chemical, association with the major minerals. In general, the trace elements in coal wastes are found in particles of elemental compositions that seem to indicate discrete mineral phases and that can be identified by direct observation with the scanning electron microscope. However, the amounts of these phases relative to the total mineral matter in the waste are too low to be detected by bulk analytical techniques such as x-ray diffraction.

Clays are the most prevalent minerals identified in Plant K materials, both by x-ray diffraction analysis and by micromineral analysis, as is typical of all coal waste samples studied. The number of occurrences of illite-type clays (identified by aluminum, silicon, and potassium peaks on the EDS) in the immediate environment of trace-element-containing particles is larger than that for kaolinite (identified by aluminum and silicon peaks but no potassium peak) in the SEM analyses. Most of the trace elements identified were found in the large matrix of clay. Nearly all the micromineral constituents identified were associated with illite-type clays. This may occur because exchange sites between the layers of such clays allow the "capture" of elements that might have passed in solution through the material at one time. Perhaps these elements later recrystallize to form the particles seen in the SEM photomicrographs.

Rare earth elements identified in these Plant K samples were lanthanum, cerium, dysprosium, and gadolinium, and always seemed to occur with phosphorous, and were apparently always in the proximity of illite-type clays. Thorium and uranium were also found in occasional particles, possibly as rare earth phosphates. Calcium occurred with phosphorous (associated with illite-type clay) and with iron and manganese. The latter occurrence could be explained if some siderite ($FeCO_3$) - dolomite [$CaMg(CO_3)_2$]-ankerite [$CA(Mg_{0.67}Fe_{0.33})(CO_3)_2$] transition were involved, especially since manganese-rich siderite was identified in several fractions by x-ray diffraction.

Iron was identified in most particles in the ratio of 1 Fe:2 S, as in pyrite, but it was also observed with no sulfur and with manganese, magnesium, or calcium instead, as in a carbonate phase. Iron also occurred with sulfur in approximately equal proportions in a few particles. This could represent either a monosulfide phase or an iron sulfate phase, which is indistinguishable by SEM/EDS.

Probable sulfates present were gypsum ($CaSO_4 \cdot 2H_20$) and barite ($BaSO_4$). The latter was predominantly in the illite-type clay.

Sulfides were present in all fractions examined. Sample 52C, sorted by gross mineral appearance as being coal with adhering pyrite, contained very "pure" pyrite and only small amounts of clay. No microminerals were noted in that fraction. Other fractions, however, contained mostly pyritic sulfides, but also contained particles of PbS, ZnS, and CuS. One particle was half PbS, half ZnS; others were mixed sulfide forms of, for example, ZnS and CuS.

Probable oxide minerals included silicon (as quartz, SiO_2), titanium (as TiO_2), and zirconium (as ZrO_2, zirconia). The common coexistence of titanium and silicon in single particles indicates the possible presence of rutilated quartz. Titanium and vanadium were found together, but the actual mineral that contained these elements could not be determined.

With a few exceptions, there were no noticeable differences in the trace minerals found from one fraction to another. The exceptions were 52C, which had numerous pyrite particles but few trace minerals, 52E, which had an abundance of siderite-type iron compared with the other fractions, and 52H, which had more rock-type (feldspathic) silicates as opposed to the clays normally found in SEM analyses of coal waste. The large pieces of granite in that fraction, atypical of coal waste material, could account for the rock silicates. (Because 52H represented only 3.2 wt% of the total waste, its atypical composition is not expected to have a significant influence on the behavior of the waste.) Samples 52D and 52F had the greatest frequency of occurrence of trace-element-containing microminerals and particles with zinc, copper, and lead. This was expected because these fractions had the most clay. However, these trace minerals were also found in other fractions, in composite sample 52A, and in the coal samples. As expected, the coals had many occurrences of organic sulfur. Although gross mineral separations greatly facilitate the concentration of the major minerals for examination by x-ray diffraction analysis, they have little effect on the microscopic particles examined by the SEM technique. This is especially true when the samples are scanned by hand, and those particles having a high density or unusual morphology (generally indicating the presence of elements with a higher atomic number than the background sea of aluminosilicate clay material) are picked for elemental analysis by the EDS. Because the particles and their immediate surrounding matrix are so small, the equivalent of dust-size particles, they could easily sift through or adhere to any type of rock, and could be in any sorted pile.

Except for the frequent occurrence of manganese-rich siderite and the atypical feldspathic material in the Plant K samples, there were no notable differences between these and other coal waste materials we have examined. Because siderite could be considered a major mineral in at least two of the Plant K fractions, the behavior of any trace element associated with siderite which, therefore, might be affected by the leachability or reactivity of siderite, might be altered from the behavior of those elements in wastes not containing iron carbonates. The elements most likely to be affected in the Plant K waste because of their association with siderite are iron, manganese, calcium, and magnesium.

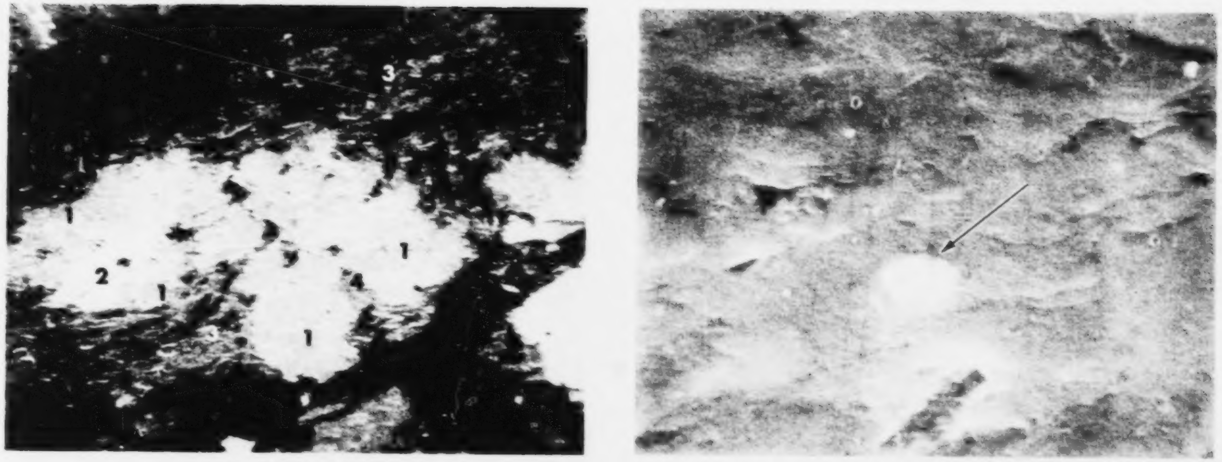
The difficulty in obtaining correlations between zinc and copper and any mineral fraction separated by size or density in coal wastes studied previously is substantiated by finding ZnS and CuS in very small particles in the Plant K waste. Such particles probably are distributed randomly among any physically separated materials. The photomicrographs in Fig. 16 illustrate the complexity of the trace element and mineral associations and the difficulty of sorting any micromineral into a "pure state."

E. Leaching Behavior

1. Static Leaching. Coal wastes, clean coal, and feed coal from Plant K were subjected to standard static leaching procedures using 5 cm^3 water/g solid.[2] The duration of these experiments ranged from 1 to 50 days. The compositions of the leachates obtained are displayed in Appendix E and in Figs. 17-19. In general, the results are consistent with those obtained from similar materials from the Illinois Basin.

The tables in Appendix E show that the pH decreases with time in all cases and that the specific conductance undergoes corresponding increases. Both trends are expected with high-sulfur coals and coal wastes and indicate that these materials have strong acid-generating tendencies. The fact that the final pH of the coal waste leachate was less than 2 suggests that this material may cause a serious acid-drainage problem if not properly disposed of.

Figure 17 shows how the element concentrations in the coal waste leachates depend on time. All the elements being studied are mobilized under acid conditions, so it is not surprising that the leachate concentrations increase with time as the pH drops. However, note that some elements show much stronger time dependences than others. In particular, arsenic, selenium, and, to a lesser degree, cadmium, increase much more rapidly in concentration than the others, and they continue to increase even after most of the other elements seem to approach equilibrium values. This suggests that the rates of dissolution for these elements are controlled by some process other than that for the remaining elements. Each of these elements tends to be associated with the pyrite-(sulfide-) containing fractions of the coal wastes. Presumably, both cadmium and arsenic are present as sulfides, and selenium is in anionic form (selenide). In each case, oxidation is required to convert the element to a water-soluble form: leaching of these elements may be controlled by the oxidation rate of the corresponding mineral instead of (or in addition to) the acidity of the leachate. Behavior should be similar from other elements in the sulfide minerals (lead, mercury, and antimony), but the importance of this mechanism depends on the solubility of the sulfide in acidic solutions, the rate of the oxidation reaction, the rate at which the ionic reactions approach equilibrium, and the fraction of the element present as

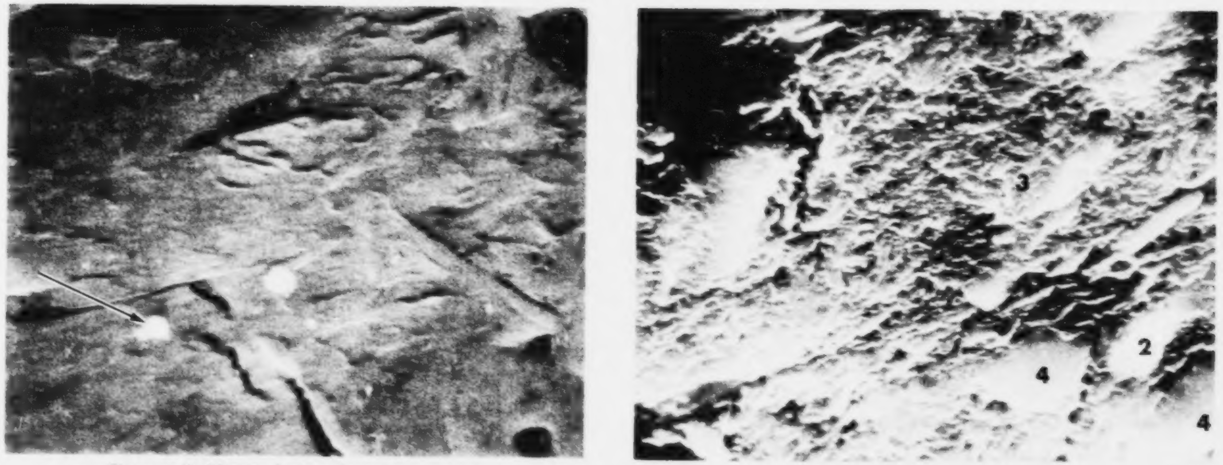


1 Fe, Mn (siderite?)
2 Pyrite
3 (KAlSi) clay
4 Si (quartz?)

188X

Rare earth (Gd, Dy, Er) Th Phosphate in a (KAlSi) clay.

3750X



Rare earth (Gd, Dy) phosphate in gypsum. The (KAlSi) clay is outside the picture.

3750X

2 Pyrite
3 (KAlSi) clay
4 Si (quartz?)

7500X

Fig. 16.

Scanning electron micrographs of selected coal waste samples from Plant K.

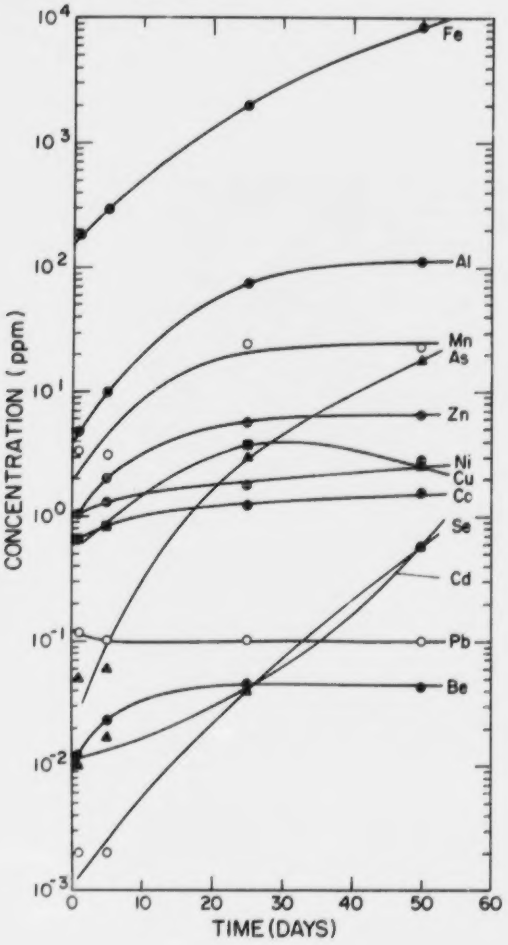


Fig. 17.
Results of static leaching experiments with coal preparation wastes from Plant K—concentrations of selected trace elements in the leachates plotted as functions of time.

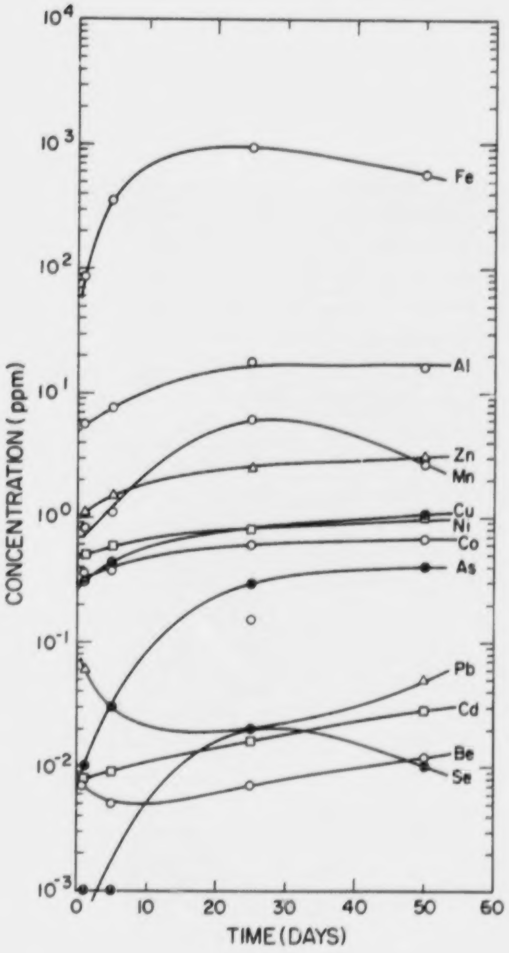


Fig. 18.
Results of static leaching experiments with feed coal from Plant K—concentrations of selected trace elements in the leachates plotted as functions of time.

the sulfide versus other chemical forms. Iron, predominantly in the form of pyrite, also falls into this category. There may be two classes of trace elements present in these wastes. Many of the elements associated with the clays and silicates may be mobilized by simple contact with acidic leaching media. However, although acidic media may be necessary to mobilize the elements in the sulfide mineral phases, acidity alone may not be sufficient, and oxidation of these minerals may be required to solubilize the trace elements because many sulfides are insoluble even in acidic media.

In Figs. 18 and 19 leaching results for the feed coal and the cleaned coal show the same general trends. The feed coal might be considered a mixture of the coal waste and the cleaned coal, so that its behavior should be between the two. This is true with regard to the time dependence of the elemental concentrations in the leachates. The coal waste has the strongest time dependence, the cleaned coal has the weakest, and the feed coal is intermediate. Concentrations of arsenic and selenium show stronger than average time dependences in the feed coal and the cleaned coal: cadmium does not. However, these experiments show that the cleaned coal

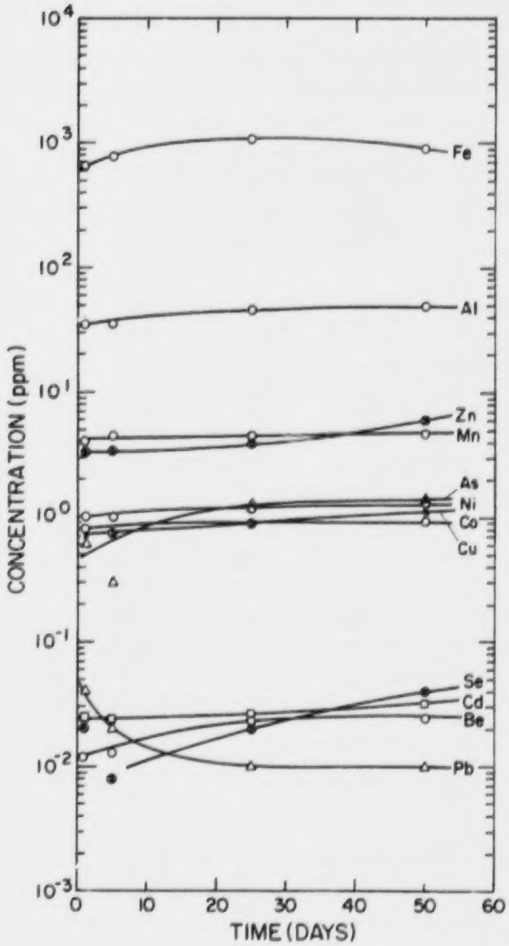


Fig. 19.

Results of static leaching experiments with cleaned coal from Plant K—concentrations of selected trace elements in the leachates plotted as functions of time.

and the coal waste give leachates with higher trace element concentrations than the feed coal. The cleaning process may affect (increase) the leachability of these trace elements, or it may be an artifact caused by the sampling process. Since the feeds to most cleaning plants vary in composition, it is difficult to know whether the outflowing process streams at a given time actually correspond to the incoming coal at the same time. This observation must be confirmed by other means before drawing conclusions.

The final element concentrations were compared with the MATE values for liquids to identify elements of environmental concern. In these comparisons, the leachate concentrations were divided by 100 to account for the effluent dilution that would occur at a disposal site.[1] The final (50-day) values were used to provide a worst-case analysis. Discharge severity factors were calculated by finding the ratio of the adjusted leachate concentration to its MATE value. Table XIV shows the results of this analysis for the Plant K materials. Iron, arsenic, nickel, manganese, and aluminum have discharge severity factors greater than unity. In addition, zinc, cadmium, and copper have discharge severity factors between 0.5 and 1.0. Any of these elements may be cause for concern under specific conditions, although iron is, by far, the worst case.

2. Dynamic Leaching. Column leaching experiments were carried out using the coal waste from Plant K. Each of four 30-cm glass columns was filled with 500 g of coal waste, previously crushed to −3/8-in. particle size. Deionized water was pumped upward through the columns at 0.5 mℓ/min. All four columns were stopped at approximately 4 ℓ total volume of effluent. Two columns were dismantled, and air was forced through the other two for 2 weeks. These columns were leached again with deionized water to collect an additional 3 ℓ of effluent from each. The specific conductance and pH of the effluents were measured as they were collected. Samples were then acidified and saved for later analysis. At the end of the experiment, selected samples were analyzed to determine their trace element contents. The results of these experiments are tabulated in Appendix E, and shown in Figs. 20 through 22.

These experiments were designed to simulate the weathering of a waste pile. For example, as coal is processed in a preparation plant and while it is being handled and transported to the waste disposal site, oxidation of the pyritic minerals and generation of acid within the waste occurs. Because water does not flow through the waste at this time, the acid accumulates until leaching occurs as the result of rain or other natural processes. Thus, the initial leachates should be much more highly contaminated than those produced after a steady state is reached. When there is no water flow (rain or other natural water) through the pile, leaching stops and accumulation of acid resumes. Subsequent leaching will again result in initially high contaminant levels. In our dynamic leaching experiments, alternating leaching and air regeneration cycles are designed to simulate this process, to provide information on the kinetics of the processes involved, to determine the relative concentrations of those contaminants released, and to identify the areas of most concern.

TABLE XIV

MEG/MATE ANALYSIS OF STATIC LEACHATES FROM PLANT K MATERIALS

Element	Concentration in Leachate (ppm)[a]			MATE Value	Discharge Severity Factors [b]		
	Coal Waste	Cleaned Coal	Feed Coal		Coal Waste	Cleaned Coal	Feed Coal
Fe	9250	890	580	0.250	370	36	23
As	18.0	1.4	0.4	0.050	3.6	0.3	0.08
Ni	2.8	1.3	1.0	0.010	2.8	1.3	1.0
Mn	23	4.7	2.6	0.10	2.3	0.5	0.3
Al	110	49	16	1.0	1.1	0.5	0.2
Zn	6.5	6.1	3.1	0.10	0.6	0.6	0.3
Cd	0.059	0.032	0.028	0.001	0.6	0.3	0.3
Cu	2.60	1.15	1.07	0.050	0.5	0.2	0.2
Se	0.57	0.04	0.01	0.025	0.2	0.02	0.004
Co	1.56	0.92	0.68	0.25	0.06	0.04	0.04
Be	0.043	0.024	0.012	0.055	0.008	0.004	0.002
Pb	<0.01	0.01	0.05	0.050	<0.002	0.002	0.01

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[a] Static leach, 50 g solids with 250 cm^3 water for 50 days.

[b] Discharge Severity Factor = (Concentration in Leachate) (0.01)÷(MATE VALUE)

Figure 20 shows the dependence of the effluent pH on the eluent volume. Initial acid contents of the leachates are very high, but they decay to more moderate values as leaching continues (consistent with the above description). Under steady flow conditions, the final acid concentration should be determined by the relative rates of acid generation within the pile and the effluent flow. Unfortunately, the leachate flow does not remain constant in a real waste pile unless the pile is in an underground aquifer. In most cases, the flow is intermittent. The air regeneration cycle shows what happens under intermittent leachate flow. Because of the large acid-generating potential of this waste, the pH of the effluent drops drastically when the leachate flow is interrupted and air flows through the waste. The only conclusion possible is that this waste may pose an acid-drainage problem of grave environmental concern unless it is disposed of in an environmentally acceptable manner.

The dependence of conductance on effluent volume is shown in Fig. 21. Conductance is a measure of the total ionic concentrations of the solution. In the case of high-sulfur coal waste leachates, the dissolved salts may depend strongly on pH, and if this is true, the conductance and the pH should behave the same. In fact, the conductance is a virtual image of the pH, clearly demonstrating that pH is a major controlling factor for the salt concentration in these leachates.

The dependences of solution concentrations of several trace elements on effluent volume are shown in Figs. 22a and b. The vertical line in each graph labeled "air regeneration" indicates the effluent volume at which the flow was interrupted and air was forced through the column. The horizontal line labeled "DS=1" shows the concentration at which the discharge severity is unity. Data points plotted above this line show contaminant levels of ecological concern. Figures 22a and b show that iron, nickel, and manganese have initial discharge severities greater than one. Of these, iron is by far the worst offender, with an initial discharge severity of nearly 100. Nickel follows with a value of 5, and manganese has a value of 2. These discharge severities decay to acceptable values, but they rise again after regeneration. Zinc, cadmium, aluminum, and copper form a group of elements having initial discharge severities between 1 and 0.5. Although this group is worthy of concern, the

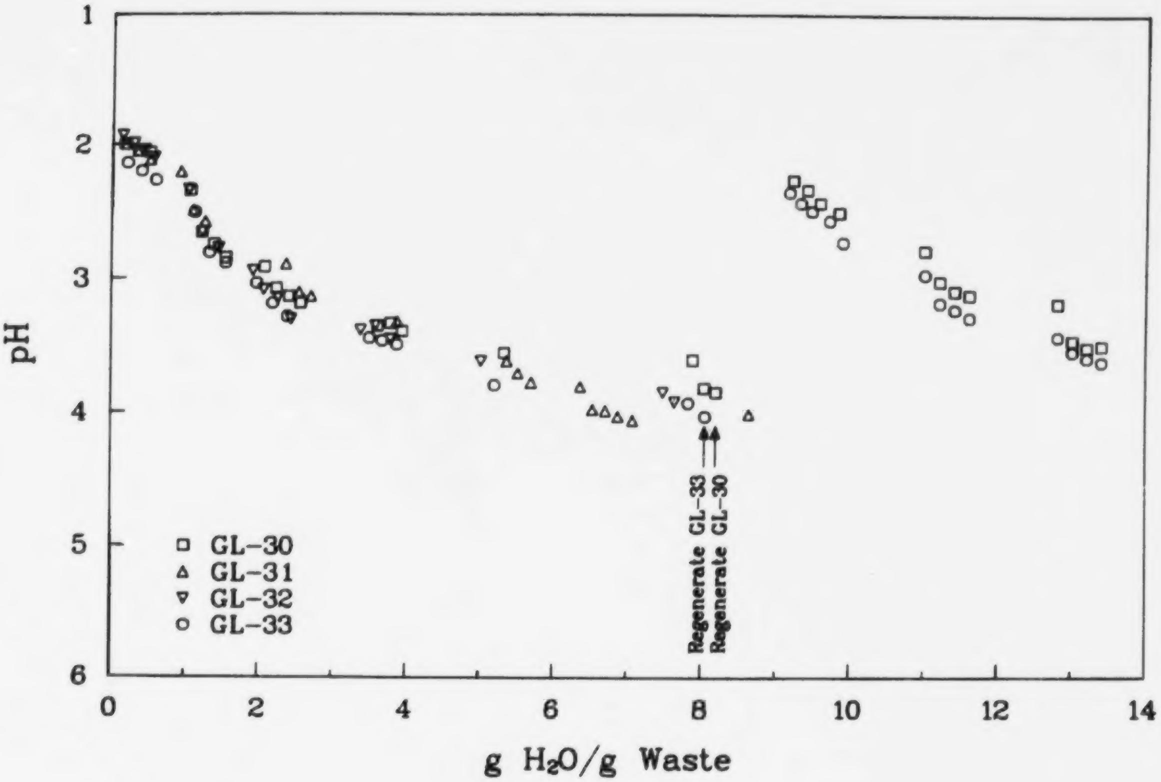

Fig. 20.
Results of dynamic leaching experiments with coal waste from Plant K—pH vs eluent volume.

discharge severities would probably not become large unless the waste underwent an unusually long regeneration cycle. Arsenic, cobalt, lead, beryllium, and selenium, with initial discharge severities less than 0.5, probably would never exceed a value of unity except under very unusual circumstances, although the highest of these, arsenic, may occasionally approach this value. Beryllium and selenium have very low discharge severities (0.02) and are unlikely to pose an environmental problem. In fact, the concentrations of these elements were near detection limits of our analytical methods.

Figures 23a and b show element concentrations in the leachates plotted as functions of pH. Circles show measurements taken before air regeneration of the columns; squares show measurements taken after regeneration. Concentrations of cadmium, lead, selenium, and beryllium are near or at the detection limits, so measurement precision is poor. Other studies of coal wastes suggest that pH is the major controlling factor in their leaching behavior. Therefore, if the system is at equilibrium, all the points should fall on a smooth curve. However, for lead, arsenic, and perhaps cobalt and aluminum, the values obtained before and after regeneration fall on different curves. Therefore, other factors, in addition to pH, control the leaching of these wastes. Some possibilities are depletion of the element in the waste, irreversible changes in the structure of the waste, or the effect of some kinetic process such as oxidation of certain minerals. Nevertheless, pH is still the *major* controlling factor in determining the leachate composition.

F. Conclusions

In general, wastes from Plant K are comparable to the high-sulfur coal wastes that we have examined from the Illinois Basin. Plant K materials are slightly lower in total sulfur and slightly higher in lithium, chlorine, arsenic, cadmium, antimony, and lutetium. They have no observable marcasite, but are high in pyrite. In addition, some of the iron is in the form of siderite, which we have

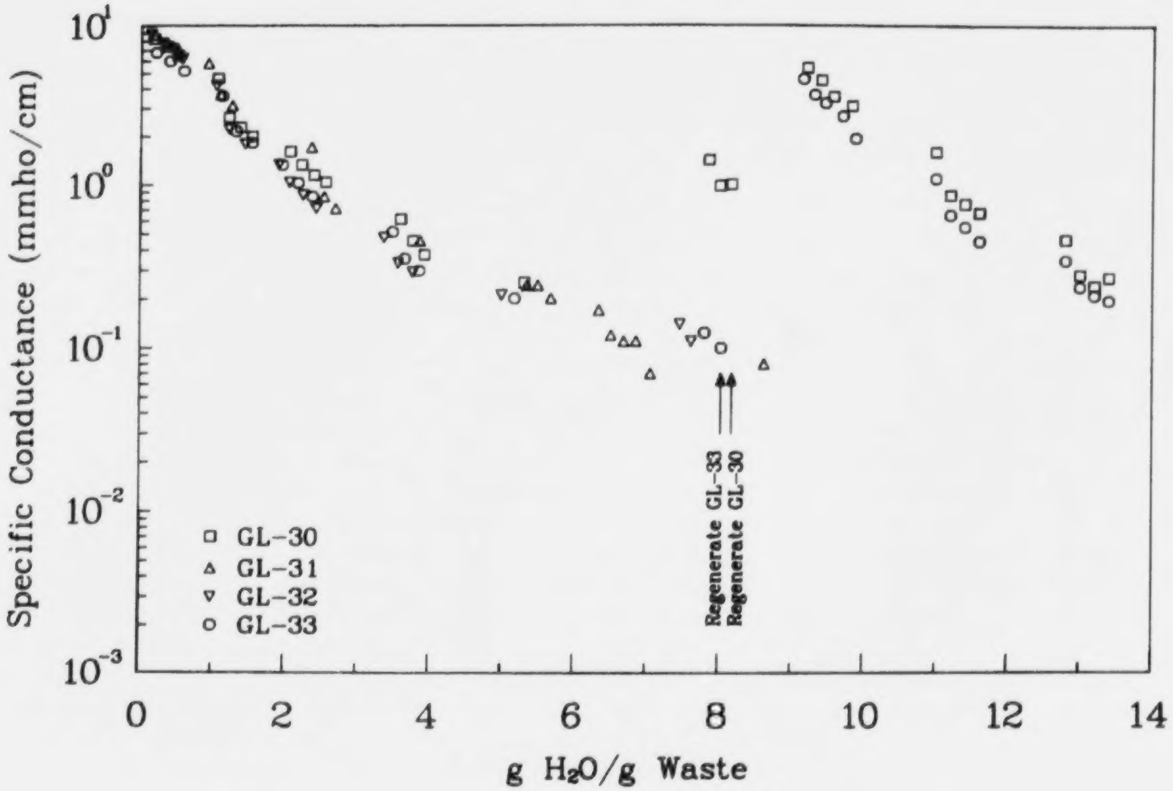

Fig. 21.
Results of dynamic leaching experiments with coal waste from Plant K—specific conductance vs eluent volume.

not previously observed in coal wastes. The calcite content is low and, as a result, these wastes have little or no self-neutralizing capacity.

The coal waste was separated into seven fractions based on the gross external appearances of the individual pieces. Elemental and mineralogical analyses of each fraction revealed some interesting correlations. Most of the trace elements with high discharge severities tend to be associated with the clay- and silicate-containing fractions. Selenium, arsenic, antimony, cadmium, and iron were predominantly found in the fractions with high pyrite contents. Several of these elements are important because of their high toxicities. Their presence in the sulfide mineral phases was expected.

Micromineralogical examination using SEM/EDS showed little difference among the fractions regarding micromineral contents, but this may have been a result of the difficulty of sampling the materials in a representative way. In general, the trace elements seem to be present as distinct micromineral phases, rather than as chemical associations with the gross minerals.

Static leaching experiments showed that acidity, specific conductivity, and trace element concentrations increase smoothly with time. Because the pH values of the leachates were very low, sometimes less than two, these wastes may pose a serious acid-drainage problem unless they are dealt with properly. Iron, arsenic, nickel, manganese, and aluminum have discharge severities greater than unity and may pose environmental problems in uncontrolled waste pile drainages. Similarly, zinc, cadmium, and copper have discharge severities between 0.5 and 1.0 and may be cause for concern under some circumstances. Concentrations of arsenic, selenium, and cadmium have much stronger time dependences than those of the other elements. Factors other than pH may control the leaching of these elements. These elements are associated with the sulfide mineral phases and probably exist as sulfides (or selenide). Consequently, their dissolution and mobilization may be limited by the oxidation rate of these minerals. Similar behavior may occur with other elements that tend to form insoluble sulfides, for example, lead and mercury.

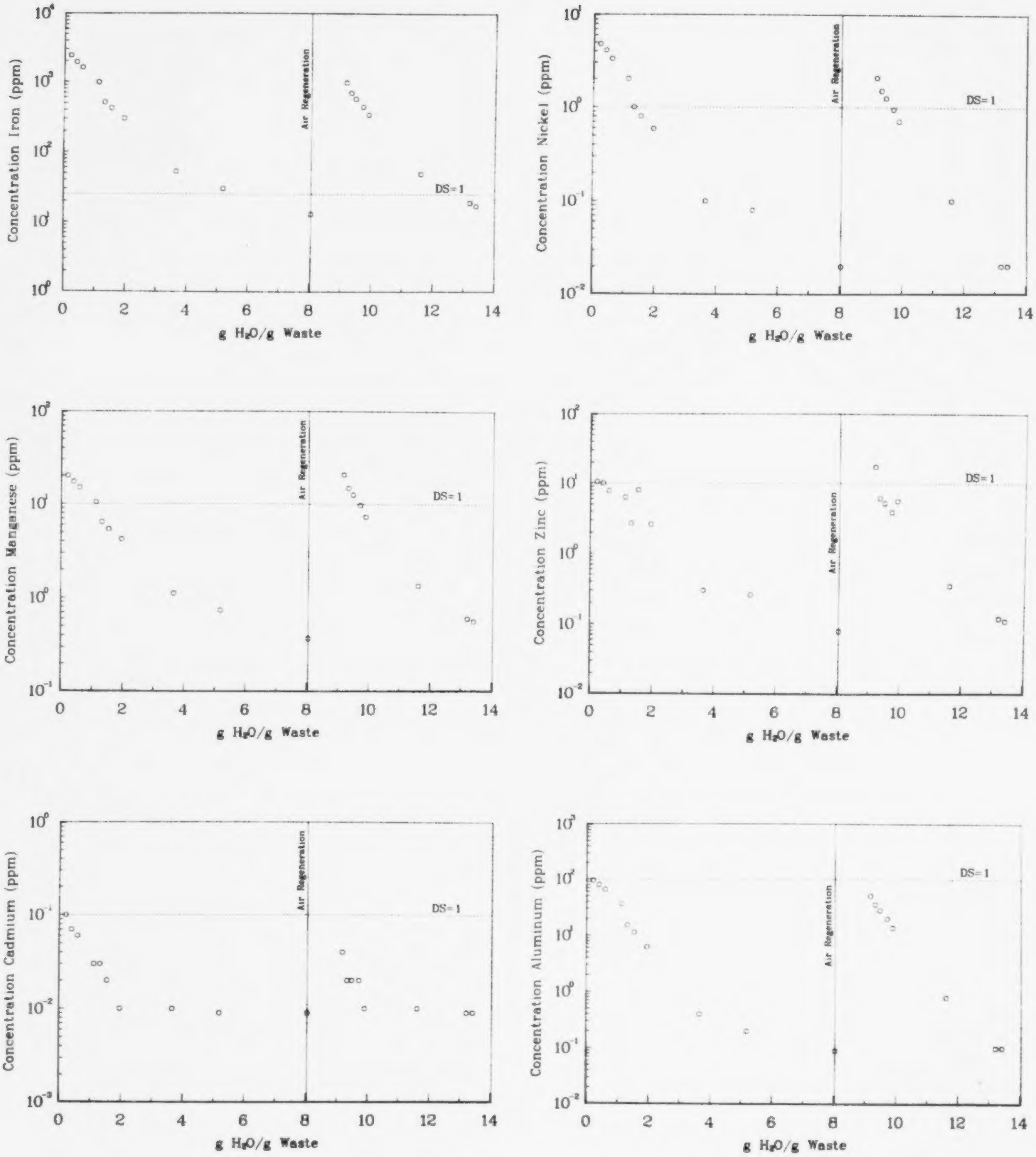

Fig. 22a.

Results of dynamic leaching experiments with coal waste from Plant K—concentrations of selected trace elements in the leachate vs eluent volume.

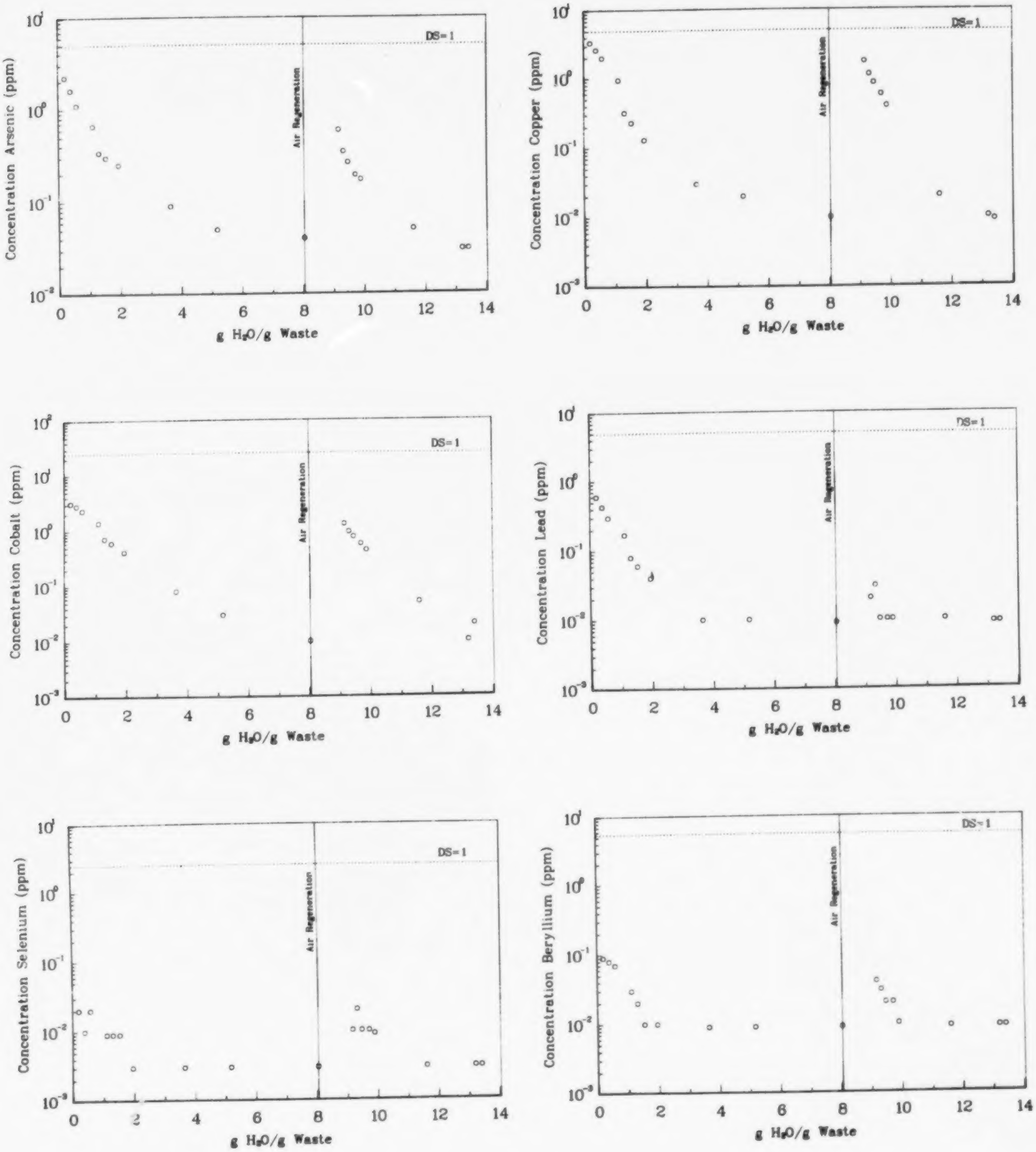

Fig. 22b.

Results of dynamic leaching experiments with coal waste from Plant K—concentrations of selected trace elements in the leachate vs eluent volume.

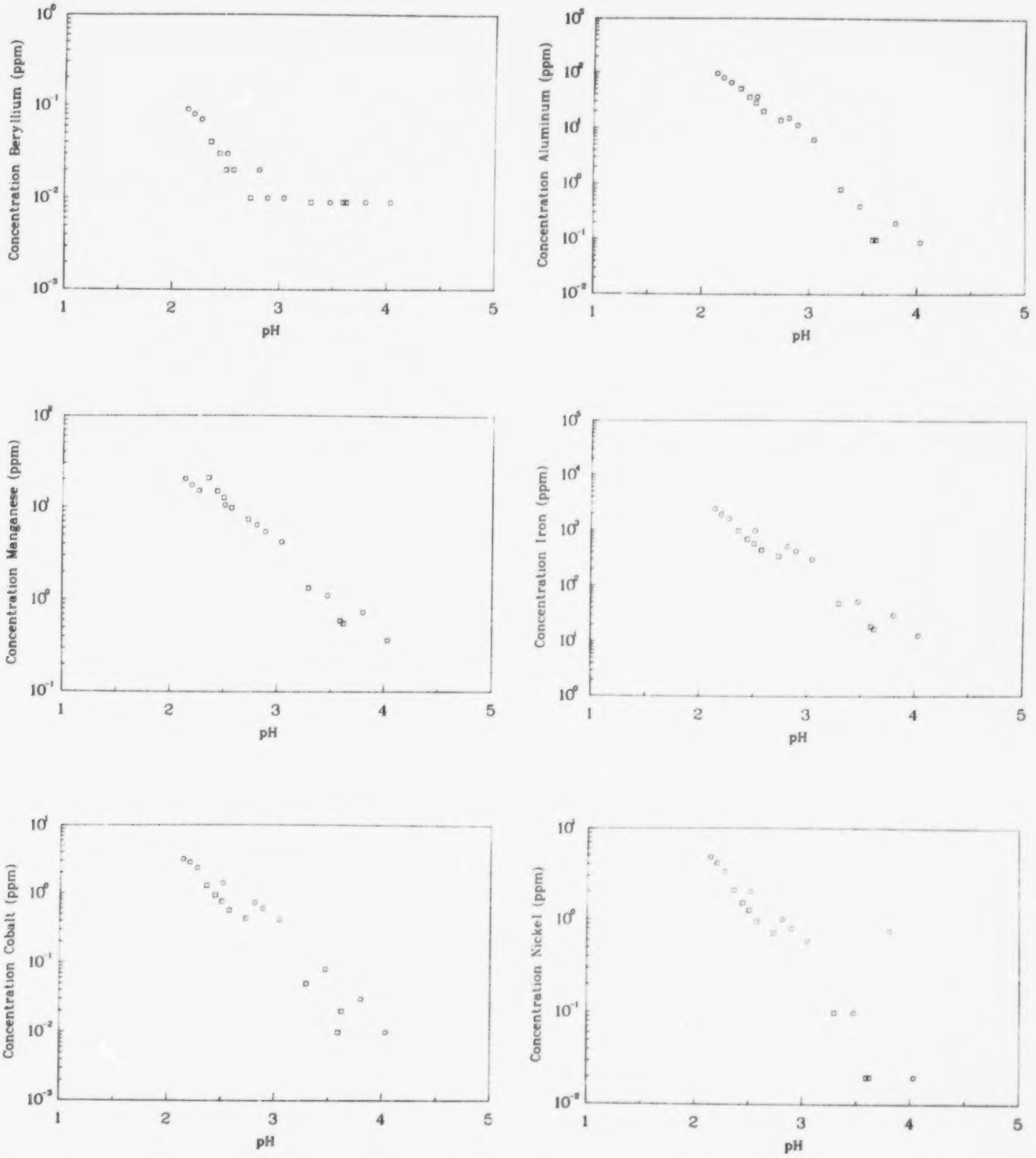

Fig. 23a.

Results of dynamic leaching experiments with coal waste from Plant K—concentrations of selected trace elements in the leachate vs pH.

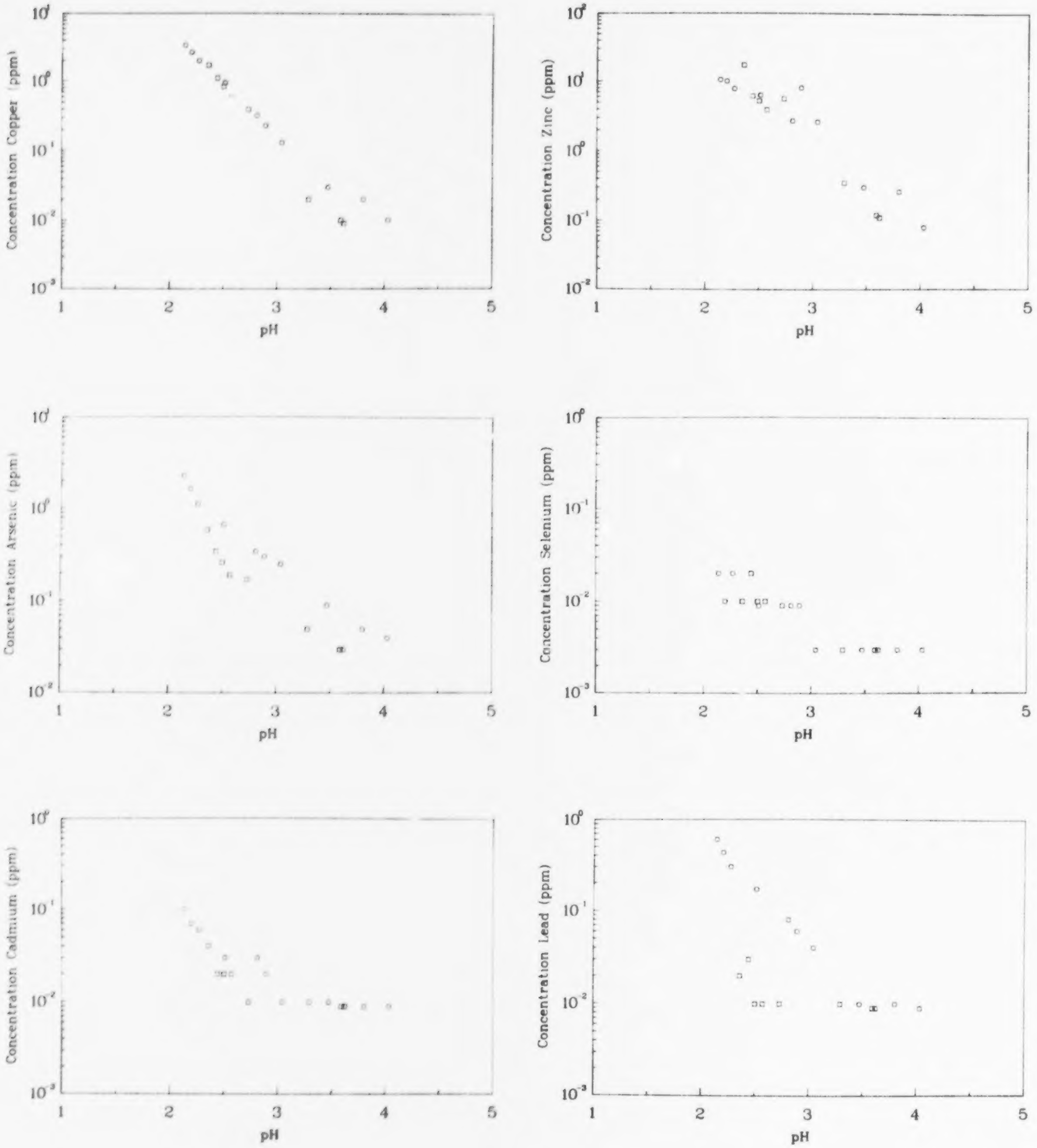

Fig. 23b.
Results of dynamic leaching experiments with coal waste from Plant K—concentrations of selected trace elements in the leachate vs pH.

Dynamic leaching experiments show that initial waste leachates are very acidic. This acidity decays to more moderate values under steady leachate flow, but high acidity recurs when the leachate flow is stopped and air is forced through the waste. Therefore, intermittent leaching of the waste can aggravate an already serious acid-drainage problem. Iron, nickel, and manganese have initial discharge severities greater than unity, but iron, with a discharge severity sometimes greater than 100, is by far the worst offender. In addition, zinc, cadmium, aluminum, and copper, with discharge severities between 0.5 and 1.0, may be cause for concern in some cases. Correlations between the element concentrations and the solution pH reveal that the pH is the major controlling factor, but that in some cases other factors are involved.

III. COMPARISONS OF EPA EXTRACTION PROCEDURE AND PAST WORK AT LOS ALAMOS

A. Background

The United States Congress, in 1976, enacted the Resource Conservation and Recovery Act (RCRA), designed to establish a comprehensive program for management of solid industrial and urban wastes. This act requires the EPA to promulgate a series of regulations that classify solid wastes as hazardous or nonhazardous, and that regulate disposal of these wastes. One criterion that determines whether a solid waste is considered hazardous because it may contaminate aqueous drainages is the results of a standard leaching procedure. This test, described in the Federal Register,[7] essentially involves leaching the solid material with deionized water under rigidly defined conditions. In the past, we have used similar procedures to study environmental weathering and leaching of these wastes; therefore, we are in a unique position to compare the RCRA leaching procedure with ours. This discussion summarizes our recent research in this area.

B. Results Obtained Using the EPA Extraction Procedure

Seven mineral wastes from coal preparation plants in the Illinois Basin, the Appalachian Region, and the Western US were leached according to the EPA extraction procedure published in the Federal Register, May 19, 1980.[7] This calls for 100 g of waste to be ground to pass through a 9.3-mm standard sieve (−3/8 in.); 1600 mℓ of deionized water is added to the waste, and the mixture is agitated for 24 h in an extractor designed to ensure that all sample surfaces are continuously brought into contact with well-mixed extraction fluid.

The pH values of the mixtures must be monitored during the extraction and, if the pH is greater than 5, adjustment must be made by addition of 0.5*N* acetic acid. After 24-h extraction, the solids are removed by filtration, and the concentrations of eight elements (silver, arsenic, barium, cadmium, chromium, mercury, lead, and selenium) in the filtrate are determined. The results of these determinations with seven coal preparation wastes are presented in Tables XV and XVI (analytical details are presented in Appendix F).

Table XV shows initial and final pH values for each sample. The pH was well below 5 in all cases except for Plant D, located in the Western US. A comparatively small amount (34 mℓ) of 0.5*N* acetic acid maintained the required pH of 5 throughout the extraction for this sample. This imposed acidic pH is probably abnormal for the western coal waste sample, but it is typical of many coal wastes from the Eastern US.

The results of the elemental analyses, Table XVI, reveal that many of the elements are present at levels below the detection limits of the analytical methods. In only three instances do any of the values exceed the Federal Primary Drinking Water Standards. These cases are the arsenic values for Plants B and K and the barium value for Plant D. However, the limits specified for these elements in nonhazardous wastes are 100 times the Primary Drinking Water Standards,[7] and all the values of Table XVI are less than 1/10 of these.

Statistical analyses were made to determine whether the analytical data could fail to detect an actual equivalence between the concentrations of the various elements and either the Primary Drinking Water Standard or the "Hazardous Waste" limit defined in the Federal Register.[7] These were done by calculating the so-called β errors, using the one-sided t-test with a 95% confidence interval. The method for this was published in Ref. 15. Some of the results of these calculations are shown in Table XVII.

Probabilities for exceeding the drinking water standards are significant only for cadmium, mercury, and lead generally, and for arsenic and barium in specific cases. The probabilities for exceeding the Hazardous Waste limits, which are 100 times the drinking water standards, are less than 0.01 in all cases.

TABLE XV

INITIAL AND FINAL pH VALUES FOR COAL WASTE LEACHATES USING THE EPA EXTRACTION PROCEDURE

	Plant[a]						
	A	B	C	D	G	I	K
pH, initial	3.1	2.8	3.3	9.6	4.1	3.1	3.3
Acetic acid added	—	—	—	35 mℓ	—	—	—
pH, final	4.2	2.2	3.2	5.0	3.8	2.6	2.7

[a] Plants A, B, C: high-sulfur, Illinois Basin waste
Plant D: low-sulfur, western waste
Plant G: low-sulfur, Appalachian waste
Plants I, K: high-sulfur, Appalachian waste

TABLE XVI

CONCENTRATIONS (ppm) OF TOXICITY INDICATOR ELEMENTS IN COAL WASTE LEACHATES

	Plant							
Element	A	B	C	D	G	I	K	HDWS[a]
Ag	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	<0.006	5.0
As	0.024	0.100	0.007	<0.001	<0.001	0.016	0.096	5.0
Ba	<0.06	0.14	0.08	1.4	0.08	<0.06	<0.06	100
Cd	<0.003	<0.004	<0.003	<0.003	<0.003	<0.003	<0.003	1.0
Cr	<0.005	0.023	0.010	<0.005	<0.005	<0.017	<0.005	5.0
Hg	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.2
Pb	<0.012	<0.012	<0.012	<0.012	<0.012	<0.012	<0.012	5.0
Se	0.0015	0.0035	0.0011	0.0016	0.0020	0.0017	0.0038	1.0

[a] 100 × Primary Drinking Water Standard.

C. Comparisons Among Different Leaching Procedures

In static leaching experiments, a fixed amount of liquid phase is kept in contact with the solid sample throughout the extraction, as opposed to allowing the liquid phase to flow through the solid. Independent variables in static experiments include the geometric surface area of the solid (mesh size), the liquid-to-solids ratio, the duration of the extraction, the degree and type of agitation used, the composition of the liquid phase, the temperature, whether the reaction mixture is open to air, and the components determined in the final leachate. Our static leaching experiments used deionized water as the liquid phase with fairly vigorous agitation (90 strokes/min, 3 in./stroke). In addition, most were done at room temperature with the extractor open to air. Except for exposure to air, these conditions are comparable to those of the EPA procedure for analysis of acidic coal wastes.

TABLE XVII

PROBABILIITIES THAT TRUE CONCENTRATIONS OF TOXICITY INDICATOR ELEMENTS EQUAL OR EXCEED FEDERAL PRIMARY DRINKING WATER STANDARDS

	Plant						
Element	A	B	C	D	G	K	I
Ag	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
As	<0.01	>0.99	<0.01	<0.01	<0.01	<0.01	>0.99
Ba	<0.01	<0.01	<0.01	>0.99	<0.01	<0.01	<0.01
Cd	<0.5	<0.8	<0.5	<0.5	<0.5	<0.5	<0.5
Cr	<0.01	0.02	<0.01	<0.01	<0.01	<0.01	<0.01
Hg	<0.5	<0.5	<0.5	<0.5	<0.5	<0.7	<0.5
Pb	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4	<0.4
Se	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

Consequently, we have only to examine the effects of the liquid-to-solid ratio, the mesh size, and the extraction time. The other variables are discussed in Sec. III.D.

Our 1-day static leach experiments are directly comparable to the EPA extraction procedure, except that we use liquid-to-solid ratios of either 4 to 1 or 5 to 1, whereas the EPA test uses a ratio of 16 to 1 during the extractions, and 20 to 1 in the final samples. The concentrations of the toxicity indicator elements in the leachates are listed in Table XVIIIa for the EPA test and in Table XIXa for our 1-day static leach. (The values in Table XVIIIa are closely related to those in Table XVI, but we adjusted them to represent the concentrations in the original leachate at a 16-to-1 liquid-to-solids ratio to eliminate the effects of the dilution of the leachate before the filtration and analysis.) If equilibrium had been reached during the extraction, the concentrations of the elements in the leachate would be independent of the liquid-to-solid ratio, provided that the supply of the original elements in the sample was not exhausted. Comparison of Tables XVIIIa and XIXa reveals that these extractions are not at equilibrium. Therefore, the element concentrations in the leachates are at least partly kinetically controlled. Under these circumstances a low liquid-to-solids ratio should be used to yield more concentrated leachates, which are easier to analyze.

A more direct comparison can be made by converting the leachate concentrations to the total amount of each element leached per unit of solid waste. These results are presented in Tables XVIIIb and XIXb. If the release of an element is strictly kinetically controlled, these data should be the same. Chromium and, to a lesser degree, cadmium compare fairly well between these two methods. However, much more arsenic was leached using the EPA method, and our procedure yielded higher lead values. We used different analytical methods for arsenic, which may explain the difference in those results, but the lead results remain unexplained.

Tables XVIIIc and XIXc show the leachate compositions as the fraction of each element in the solid before dissolution. These results exactly parallel those in Tables XVIIIb and XIXb. However, it is interesting that cadmium is highly mobile, with large percentages being extracted, whereas other elements are extracted to much lesser degrees.

Results of extractions done on 20-mesh samples are shown in Tables XXa-c. In general, these results are much the same as those of the −3/8-in. samples described in Tables XIXa-XIXc. Reduction of the particle size from 3/8 in. to 20 mesh means a substantial increase in the geometric surface area, so either the actual effective surface area is much larger than the geometric surface, or the surface area does not affect the leaching behaviors of the elements. The former conclusion seems more likely.

Longer term static leaches are summarized in Tables XXIa-XXIc. In most cases, the amounts of leached elements remained constant or increased with duration of extraction. Although this agrees with our concept of the way leaching works, the differences between the 1-day

TABLE XVIIIa

ADJUSTED* LEACHATE COMPOSITIONS OBTAINED USING THE RCRA LEACHING PROCEDURE FOR COAL WASTE SAMPLES (ppm)

	Plant						
Element	A	B	C	D	G	I	K
Ag	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008	<0.008
As	0.030	0.125	0.009	<0.001	<0.001	0.020	0.120
Ba	<0.075	0.175	0.100	0.075	0.100	<0.075	<0.075
Cd	<0.004	<0.005	<0.004	<0.004	<0.004	<0.004	<0.004
Cr	<0.006	0.029	0.012	<0.006	<0.006	<0.021	<0.006
Hg	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
Pb	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015	<0.015
Se	0.0019	0.0044	0.0014	0.0020	0.0025	0.0021	0.0048
pH	4.2	2.2	3.2	5.0	3.8	2.6	2.7

*Adjusted to reflect original leachate composition at 16-to-1 liquid-to-solids ratio, before dilution to the final 20-to-1 ratio.

TABLE XVIIIb

LEACHATE COMPOSITIONS OBTAINED USING RCRA LEACHING PROCEDURE FOR COAL WASTE SAMPLES. RESULTS EXPRESSED AS MILLIGRAM ELEMENT LEACHED PER KILOGRAM SOLID WASTE

	Plant						
Element	A	B	C	D	G	I	K
Ag	<0.120	<0.120	<0.120	<0.120	<0.120	<0.120	<0.120
As	0.480	2.00	0.140	<0.020	<0.020	0.320	1.92
Ba	<1.20	2.80	1.60	1.20	1.60	<1.20	<1.20
Cd	<0.060	<0.080	<0.060	<0.060	<0.060	<0.060	<0.060
Cr	<0.100	0.460	0.200	<0.100	<0.100	<0.340	<0.100
Hg	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020	<0.020
Pb	<0.240	<0.240	<0.240	<0.240	<0.240	<0.240	<0.240
Se	0.030	0.070	0.022	0.032	0.040	0.34	0.075
pH	4.2	2.2	3.2	5.0	3.8	2.6	2.7

TABLE XVIIIc

LEACHATE COMPOSITIONS OBTAINED USING RCRA LEACHING PROCEDURE FOR COAL WASTE SAMPLES. RESULTS EXPRESSED AS THE PERCENT OF THE ELEMENT ORIGINALLY PRESENT THAT APPEARS IN THE LEACHATE

	Plant						
Element	A	B	C	D	G	I	K
Ag	—	--	—	<32	—		
As	0.86	2.1	0.64	—	<0.11		
Ba	—	—	—	—	—		
Cd	<25	<20	<5.4	<9.7	<18		
Cr	<0.17	0.74	0.29	<0.07	<0.11		
Hg	—	—	—	—	—		
Pb	<0.49	<0.71	<0.48	<0.86	<1.0		
Se	0.32	1.1	0.26	—	—		
pH	4.2	2.2	3.2	5.0	3.8	2.6	2.7

TABLE XIXa

LEACHATE COMPOSITIONS OBTAINED FROM ONE-DAY SHAKER LEACHES OF COAL WASTE SAMPLES (−3/8-in.) (ppm)

	Plant						
Element	A	B	C	D	G	I	K
Ag	—	—	—			—	—
As	0.008	—	0.004			—	0.054
Ba	—	—	—			—	—
Cd	0.0014	0.024	0.020			0.015	0.010
Cr	0.001	0.060	0.032			0.094	—
Hg	—	—	—			—	—
Pb	0.048	0.300	0.32			—	0.15
Se	—	—	—			—	0.002
pH	7.1	2.2	3.5			2.6	3.0

TABLE XIXb

LEACHATE COMPOSITIONS OBTAINED FROM ONE-DAY SHAKER LEACHES OF COAL WASTE SAMPLES (−3/8-in.). RESULTS EXPRESSED AS MILLIGRAMS ELEMENT LEACHED PER KILOGRAM SOLID WASTE

	Plant						
Element	A	B	C	D	G	I	K
Ag	—	—	—			—	—
As	0.04	—	0.02			—	0.270
Ba	—	—	—			—	—
Cd	0.0068	0.12	0.10			0.075	0.050
Cr	0.005	0.30	0.16			0.470	—
Hg	—	—	—			—	—
Pb	0.240	1.5	1.6			—	0.750
Se	—	—	—			—	0.010
pH	7.1	2.2	3.5			2.6	3.0

TABLE XIXc

LEACHATE COMPOSITIONS OBTAINED FROM ONE-DAY SHAKER LEACHES OF COAL WASTE SAMPLES (−3/8-in.). RESULTS EXPRESSED AS THE PERCENT OF THE ELEMENT ORIGINALLY PRESENT THAT APPEARS IN THE LEACHATE

	Plant						
Element	A	B	C	D	G	I	K
Ag	—	—	—				
As	0.07	—	0.09				
Ba	—	—	—				
Cd	2.8	30	8.9				
Cr	0.008	0.48	0.23				
Hg	—	—	—				
Pb	0.49	4.4	3.2				
Se	—	—	—				
ph	7.1	2.2	3.5				

TABLE XXa

LEACHATE COMPOSITIONS OBTAINED FROM ONE-DAY SHAKER LEACHES OF COAL WASTE SAMPLES (–20 MESH) (ppm)

	Plant						
Element	A	B	C	D	G	I	K
Ag	<0.008	—	<0.008		—	—	
As	<0.008	—	<0.004		—	—	
Ba	—	—	—		—	—	
Cd	2.9	48	8.9		9.3		
Cr	<0.001	0.156	0.032		0.0018	0.080	
Hg	<0.20	—	<0.20		—	—	
Pb	0.048	0.320	0.320		—	—	
Se	—	—	—		—	—	
pH	7.1	2.2	3.5		4.3	3.2	

TABLE XXb

LEACHATE COMPOSITIONS OBTAINED FROM ONE-DAY SHAKER LEACHES OF COAL WASTE SAMPLES (–20 MESH). RESULTS EXPRESSED AS MILLIGRAMS ELEMENT LEACHED PER KILOGRAM SOLID WASTE

	Plant						
Element	A	B	C	D	G	I	K
Ag	<0.040	—	<0.040		—	—	
As	<0.040	—	<0.020		—	—	
Ba	—	—	—		—	—	
Cd	0.0070	0.190	0.100		0.031	0.10	
Cr	<0.005	0.780	0.160		0.007	0.40	
Hg	<1.00	—	<1.00		—	—	
Pb	0.24	1.60	1.60		—	—	
Se	—	—	—		—	—	
pH	7.1	2.2	3.5		4.3	3.2	

TABLE XXc

LEACHATE COMPOSITIONS OBTAINED FROM ONE-DAY SHAKER LEACHES OF COAL WASTE SAMPLES (–20 MESH). RESULTS EXPRESSED AS THE PERCENT OF THE ELEMENT ORIGINALLY PRESENT THAT APPEARS IN THE LEACHATE

	Plant						
Element	A	B	C	D	G	I	K
Ag	—	—	—		—		
As	<0.07	—	<0.09		—		
Ba	—	—	—		—		
Cd	2.9	48	8.9		9.3		
Cr	<0.008	1.2	0.23		0.008		
Hg	—	—	—		—		
Pb	0.49	4.7	3.2		—		
Se	—	—	—		—		
pH	7.1	2.2	3.5		4.3		

TABLE XXIa

LEACHATE COMPOSITIONS OBTAINED FROM LONG-TERM SHAKER LEACHES OF COAL WASTE SAMPLES (–3/8-in.) (ppm)

	Plant						
Element	A	B	C	D	G	I	K
Days	28	22	28			25	25
Ag	—	—				—	—
As	0.008	—	0.175			—	3.0
Ba	—	—	—			—	—
Cd	0.0003	0.035	0.124			0.01	0.041
Cr	0.0012	0.116	0.240			0.10	—
Hg	—	—	—			—	—
Pb	0.006	0.280	0.360			—	0.004
Se	—	—	—			—	0.036
pH	7.6	1.9	1.9			2.2	2.0

TABLE XXIb

LEACHATE COMPOSITIONS OBTAINED FROM LONG-TERM SHAKER LEACHES OF COAL WASTE SAMPLES (–3/8-in.) RESULTS EXPRESSED AS MILLIGRAMS ELEMENT LEACHED PER KILOGRAM SOLID WASTE

	Plant						
Element	A	B	C	D	G	I	K
Days	28	28	28			25	25
Ag	—	—	—			—	—
As	0.04	—	0.88			—	15.0
Ba	—	—	—			—	—
Cd	0.0014	0.18	0.62			0.05	0.205
Cr	0.006	0.58	1.20			0.50	—
Hg	—	—	—			—	—
Pb	0.030	1.40	1.80			—	0.020
Se	—	—	—			—	0.180
pH	7.6	1.9	1.9			2.2	2.0

TABLE XXIc

LEACHATE COMPOSITIONS OBTAINED FROM LONG-TERM SHAKER LEACHES OF COAL WASTE SAMPLES (–3/8-in.) RESULTS EXPRESSED AS THE PERCENT OF THE ELEMENT ORIGINALLY PRESENT THAT APPEARS IN THE LEACHATE

	Plant						
Element	A	B	C	D	G	I	K
Days	28	28	28			25	25
Ag	—	—	—				
As	0.071	—	4.0				
Bg	—	—	—				
Cd	0.583	45.0	55.4				
Cr	0.010	0.935	1.74				
Hg	—	—	—				
Pb	0.061	4.12	3.60				
Se	—	—	—				
pH	7.6	1.9	1.9			2.2	2.0

and the multiday leaches are small. This suggests that most of the action, at least for arsenic, cadmium, chromium, and lead, occurs in the early part of the experiment (the first 24 h).

Our static leaching experiments were designed to determine materials that might be leached from a coal waste: our dynamic (column) leaching experiments were designed to simulate the weathering of an exposed waste pile. We wanted to study the leaching of elements as a function of time and to discover the effects of intermittent leaching. Although these experiments are more difficult to compare with the EPA procedure than the static leaches, we compared them by integrating the concentration-versus-volume curve in each element to a volume representing a 16-to-1 liquid-to-solids ratio. This gives the total amount of an element extracted in that volume. From these results, we calculated the amounts extracted per unit solids shown in Table XXIIb, and from those values, we derived the results shown in Tables XXIIa and c. Most of the extraction occurs early in the experiment, so that the choice of the upper volume limit to the integration does not drastically affect the results. In general, the column leaching experiments show higher extraction efficiencies than the static experiments, especially for arsenic and, to lesser degrees, for cadmium and chromium. Lead shows the reverse trend, possibly because of reprecipitation caused by the increase in pH with time.

In summary, results of the EPA leaching procedure agree with results of our procedure to the extent to which these methods can be compared. The major difference between the procedures (in the case of acidic coal preparation wastes) is the higher liquid-to-solids ratio used in the EPA method. This high ratio dilutes the leachate and makes chemical analyses more difficult. With nonacidic coal wastes, another difference is that acetic acid is added to the extraction mixture in the EPA method. For coal wastes that are not naturally acidic, this creates an artificial environment and complicates interpretation of the results.

TABLE XXIIa

LEACHABILITIES OF SELECTED ELEMENTS FROM COAL WASTE SAMPLES (−3/8-in.) OBTAINED FROM CONTINUOUS COLUMN LEACHING EXPERIMENTS.
(ppm for 16 ℓ water per kg solid)

	Plant			
Element	A	B	C	G
Ag	—	—	—	—
As	0.016	0.34	0.50	—
Ba	—	—	—	—
Cd	0.0048	0.016	0.0072	0.0026
Cr	0.031	0.021	0.050	0.0080
Hg	—	—	—	—
Pb	0.014	0.022	0.0075	—
Se	—	—	—	—
pH	2.9-7.7	1.7-3.4	2.4-3.8	2.9-4.0

TABLE XXIIb

LEACHABILITIES OF SELECTED ELEMENTS FROM COAL WASTE SAMPLES (−3/8-in.) OBTAINED FROM CONTINUOUS COLUMN LEACHING EXPERIMENTS. RESULTS EXPRESSED AS MILLIGRAM ELEMENT LEACHED PER KILOGRAM SOLID WASTE

	Plant			
Element	A	B	C	G
Ag	—	—	—	—
As	0.26	5.3	0.80	—
Ba	—	—	—	—
Cd	0.077	0.26	0.12	0.042
Cr	0.49	0.39	0.80	0.13
Hg	—	—	—	—
Pb	0.22	0.35	0.12	—
Se	—	—	—	—
pH	2.9-7.7	1.7-3.4	2.4-3.8	2.9-4.0

TABLE XXIIc

LEACHABILITIES OF SELECTED ELEMENTS FROM COAL WASTE SAMPLES (−3/8-in.) OBTAINED FROM CONTINUOUS COLUMN LEACHING EXPERIMENTS RESULTS EXPRESSED AS PERCENT OF THE ELEMENT ORIGINALLY PRESENT THAT APPEARS IN THE LEACHATE

	Plant			
Element	A	B	C	G
Ag	—	—	—	—
As	0.46	5.7	3.6	—
Ba	—	—	—	—
Cd	32	66	10	13
Cr	0.82	6.4	1.2	0.14
Hg	—	—	—	—
Pb	0.44	1.0	0.24	—
Se	—	—	—	—
pH	2.9-7.7	1.7-3.4	2.4-3.8	2.9-4.0

D. EPA Leaching Procedure as Applied to Coal Wastes

The EPA leach test is designed to satisfy a regulatory need to classify solid wastes as hazardous or not. As such, it must apply to a wide variety of wastes, including municipal, chemical, and industrial by-products, whose properties and chemical behaviors may differ substantially. It is unlikely that any single test can be entirely appropriate in all cases, and thus, it is important to understand the limitations of the test for various types of waste. The following discussion concerns our observations on the applicability of the EPA leaching test to coal preparation wastes. The most important question is whether the EPA leaching test accurately indicates whether a given waste can harm the environment.

Studies have revealed that the chemical components with the highest discharge severities in leachates from coal preparation wastes are iron, aluminum, nickel, manganese, zinc, copper, and cadmium, as well as the acidity.[1-3] The elements addressed in the EPA leaching test are those included in the Federal Primary Drinking Water Standards (silver, arsenic, barium, cadmium, chromium, mercury, lead, and selenium). The only element common to these two groups is cadmium. Iron has by far the highest discharge severity, based on the MEG/MATE system,[5] followed roughly in order by the other elements listed. Some of the elements included in the EPA procedure, notably silver, mercury, and barium are typically present at levels below the detection limits of the methods used for the analysis of the leachates. Furthermore, the parent coal waste materials often contain these elements in such minimal quantities that we have rarely attempted to determine them in our research on coal waste leaching behavior. Consequently, in the case of typical coal preparation wastes, we conclude that the present EPA leaching test does not address the elements of real concern. If the elements in the Secondary Drinking Water Standards were included, the test would be markedly improved because iron, manganese, zinc, and copper would be covered. Only aluminum and nickel, elements of potential concern, would not be analyzed in the EPA leaching test.

In analysis of acidic coal wastes, the leachates are sufficiently acid so that no acetic acid additions are needed. Under these circumstances, the EPA test is essentially a water leach and reasonably simulates the acid-base conditions expected in a stagnant coal waste pile. Acidic coal wastes are the most abundant type and represent the wastes of most concern in the Eastern US coal fields, so this test is appropriate. However, alkaline coal wastes, typically from the Western US, are treated differently in the EPA test. These wastes are acidified to a pH of 5 with acetic acid and subjected to an artificial environment that they are unlikely to encounter under normal circumstances. We believe this test is unnecessarily severe for those elements mobilized under acidic conditions, and it ignores the possible effects of elements such as selenium and arsenic, which may be alkaline mobile.

Because small particles have a higher geometric surface area per unit mass than large particles, the results of a leaching experiment should depend on the size of the particles in the solid sample. However, our experience with coal wastes shows that particle size does not strongly affect the results of leaching experiments. Therefore, we chose the most convenient size for this type of waste [9.3 mm (−3/8 in.)].

Agitation of the sample during the leaching procedure is most important. The EPA test procedure calls for vigorous agitations, which, in our opinion, is preferable to stagnant leaching: a vigorous agitation is easier to define and reproduce from one experiment to the next and among different laboratories.

Duration of leaching, necessarily a compromise, must be long enough to allow any chemical reactions to proceed to a reasonable degree, and yet short enough to complete the experiment in a reasonable time. With high-sulfur coal wastes with no self-neutralizing capacity, the 24-h extraction time seems reasonable. However, some materials may not become severely acidic for several days or even weeks. This delay may be caused by the presence of carbonate minerals acting as *in situ* neutralizing agents, which must be used up before the pH can become very acidic. Such a delay in the acid-releasing character of a coal waste could result in a toxic material being erroneously classified as nonhazardous. The only straightforward way to avoid this is to run leaching experiments for longer periods of time. In addition, there is the question of how the aging of a refuse pile might affect its leaching behavior. This may be outside the purview of a regulatory test procedure, and is a problem that can only be addressed by careful research and understanding of the chemistry of the refuse material.

One factor important in the case of coal wastes (but possibly unimportant for other types of solid wastes) is the presence of air during the leaching process. The leachates from coal wastes are acidic because the oxidation of pyrite yields sulfuric acid as a by-product. If access of air to the solid is restricted, less oxidation occurs and the leachates are less acidic. In a 24-h leaching experiment, most of the acid involved was generated before the actual leach was begun, so access to air may not be important. However, in longer leaching experiments, the generation of acid during the experiment may be significant and restriction of the air intake may lead to artificially low results.

With reference to coal waste samples, liquid-to-solid ratios of 20 to 1 for the final analysis often tax the detection limits of the analytical procedures. A lower liquid-to-solids ratio, for example, 4 or 5 to 1, would allow greater confidence in the analytical results and their implications concerning pollution potentials.

Finally, we offer one comment on the mechanical aspects of the extraction procedure. To facilitate the rapid separation of the leachate from the solid residue, thus eliminating long contact times of leachate and residue after the 24-h agitation period, we have found it advantageous to use a prefiltering step with a hard ashless filter paper (Whatman 541) and a Buchner porcelain funnel before final filtration through a Millipore 0.45-μm filter. Even a glass fiber prefilter, as mentioned in the extraction procedure, offers little relief from prolonged separations of materials containing clays, and the prefiltering with the paper is much more rapid than the centrifuge method described in the EPA test procedure.

E. Summary and Conclusions

Mineral wastes from seven coal preparation plants, located in various parts of the country, have been leached in accordance with the EPA extraction procedure published in the Federal Register dated May 19, 1980.[7] According to the criteria set forth in this procedure, all the coal wastes are nonhazardous. The probability that any of the eight elements examined might exceed the levels set forth in the procedure is less than 1%. The probabilities of the elements exceeding the Federal Primary Drinking Water standards are significant only for cadmium, mercury, and lead.

Compared with leaching tests we have used over the past several years on coal wastes, the EPA test gives similar results for those elements examined. The primary differences between our procedure and that of the EPA are the use of a higher liquid-to-solids ratio in the EPA test and their requirement that alkaline systems be acidified with acetic acid.

With respect to coal preparation wastes we can make the following comments concerning the EPA extraction procedure.

- Iron, aluminum, nickel, and manganese, which have the highest discharge severities in coal waste leachates, are not addressed by the method.
- We believe that the acidification of nonacidic materials is inappropriate in the case of coal wastes.
- Filtration time can be significantly shortened by introducing a prefiltering step before filtration through the Millipore filter.

We also question whether longer extraction times should be considered and whether the extraction vessel should be left open to the air.

REFERENCES

1. E. M. Wewerka, J. M. Williams, L. E. Wangen, J. P. Bertino, P. L. Wanek, J. D. Olsen, E. F. Thode, and P. Wagner, "Trace Element Characterization of Coal Wastes, Third Annual Progress Report," Los Alamos Scientific Laboratory report LA-7831-PR, EPA-600/7-79-144 (June 1979).

2. E. M. Wewerka, J. M. Williams, N. E. Vanderborgh, A. W. Harmon, P. Wagner, P. L. Wanek, and J. D. Olsen, "Trace Element Characterization of Coal Wastes, Second Annual Progress Report," Los Alamos Scientific Laboratory report LA-7360-PR, EPA-600/7-78-028a (July 1978).

3. E. M. Wewerka and J. M. Williams, "Trace Element Characterization of Coal Wastes, First Annual Report," Los Alamos Scientific Laboratory report LA-6835-PR, EPA-600/7-78-028 (March 1978).

4. J. M. Williams, J. P. Bertino, M. M. Jones, P. Wagner, P. L. Wanek, L. E. Wangen, and E. M. Wewerka, "Trace Element Characterization of Coal Wastes, Fourth Annual Progress Report," Los Alamos National Laboratory report LA-8275-PR, EPA-600/7-81-073 (April 1981).

5. J. G. Cleland and G. L. Kingsbury, "Multimedia Environmental Goals for Environmental Assessment." Vols. I and II, Environmental Protection Agency reports EPA-600/7-77-136a and EPA-600/7-77-136b (November 1977).

6. J. C. Westall, J. L. Zachary, and F. M. M. Morel, "MINEQL: A Computer Program for the Calculation of Chemical Equilibrium Composition of Aqueous System," Massachusetts Institute of Technology, Department of Civil Engineering, Technical Note No. 18 (July 1976).

7. Federal Register **45** (98), 33127 (May 19, 1980).

8. R. Rao Gadde and H. A. Laitinen, "Studies of Heavy Metal Adsorption by Hydrous Iron and Manganese Oxides," Anal. Chem. **46**, 2022 (1974).

9. E. A. Jenne, "Controls on Mn, Fe, Co, Ni, Cu and Zn Concentrations in Soils and Water: The Significant Role of Hydrous Mn and Fe Oxides," in *Trace Inorganics in Water*, R. F. Gould, Ed. (American Chemical Society, 1968), Chap. 21, pp. 337-387.

10. R. O. James and T. W. Healy, "Adsorption of Hydrolyzable Metal Ions at the Oxide-Water Interface I. Co(II) Adsorption on SiO_2 and TiO_2 as Model Systems," J. Colloid Interface Sci. **40**, 42 (1972).

11. E. F. Thode, J. M. Williams, E. M. Wewerka, and P. Wagner, "Costs of Coal and Electric Power Production—The Impact of Environmental Control Technologies for Coal-Cleaning Plants," Los Alamos Scientific Laboratory report LA-8039-MS (October 1979).

12. E. M. Wewerka, J. M. Williams, N. E. Vanderborgh, P. Wagner, P. L. Wanek, and J. D. Olsen, "Trace Element Characterization and Removal/Recovery from Coal and Coal Wastes: Progress Report for the Period October 1, 1976 to December 31, 1976," Los Alamos Scientific Laboratory report LA-6933-PR (October 1977).

13. J. M. Williams, "Qualitative and Quantitative X-Ray Mineralogy: A Layman's Approach," Los Alamos Scientific Laboratory report LA-8409-MS (June 1980).

14. J. M. Williams, N. E. Elliott, E. A. Hakkila, W. B. Hutchinson, L. S. Levinson, R. D. Reiswig, W. O. Wallace, E. M. Wewerka, and W. F. Zelezny, "Coal Preparation Waste Micromineralogy," Los Alamos Scientific Laboratory report LA-8474-MS (August 1980).

15. M. G. Natrella, "Experimental Statistics," National Bureau of Standards Handbook 91, US Government Printing Office (1966), pp. 3-13.

APPENDIX A

RESULTS OF LIME AND LIME/LIMESTONE TREATMENT EXPERIMENTS

Detailed descriptions of the procedures used in this experiment were published in Ref. 4 (main text); however a brief summary is provided here. Results are presented in Tables A-I through -VII.

Three 55-gal. drums of Plant M, high-sulfur, Illinois Basin coal preparation waste were crushed to −3/8 in. without prior drying. Scoops of material from each barrel were placed in sequence into six empty barrels fitted with plastic liners until each barrel held 250 lb of material. We added 30 ℓ of deionized water to each barrel and tumbled the barrel for 5 min at 15 rpm. After the barrels stood for several days, excess water (approximately 8 ℓ) was siphoned off and analyzed for acidity. The leachates had pH values from 2.8 to 2.9 and were 0.045 molar in acid. We added a slurry (38 to 50% solids) of lime to each barrel. This slurry was blended into the waste slurry by tumbling the barrel at 15 rpm for 2 min. In one case, limestone was later added and blended. (Each mixture settled for 4 to 9 days while other barrels were being prepared and used.) After settling, excess water was siphoned off, and the slurry was sieved through a muslin filter into a 90- by 150- by 25-cm-deep polyethylene tub and spread evenly to allow further water drainage.

The drained lime/limestone/waste slurries were portioned into several groups. The first six portions (1/10

TABLE A–I

RESULTS OF LABORATORY WEATHERING EXPERIMENTS USING HIGH–SULFUR COAL PREPARATION WASTE TREATED WITH 0.17% LIME

Time (Weeks)	Volume (ℓ)	Cum Volume (ℓ)	Cum Vol[*]/ Mass Waste (cm^3/g)	pH	Cond (mmho/cm)	Total Fe (mg/cm^3)	Fe (II) (mg/cm^3)
3	0.65	0.65	0.057	2.37	6.80	3.75	2.00
4	0.75	1.40	0.123	2.23	7.50	5.18	2.25
5	1.06	2.46	0.216	2.16	8.70	8.47	2.95
6	0.92	3.38	0.296	2.17	9.35	8.50	3.94
7	1.04	4.42	0.388	2.18	12.0	9.70	3.64
8	1.04	5.46	0.479	2.17	12.5	12.3	3.72
9	1.00	6.46	0.567	1.96	12.8	14.4	4.86
10	0.80	7.26	0.637	1.73	19.0	21.4	7.98
11	1.10	8.36	0.733	1.98	11.0	11.6	3.84
12	1.03	9.39	0.824	1.84	13.0	11.8	3.45
13	0.88	10.27	0.901	1.77	16.0	12.8	4.42
15	4.08	14.35	1.26	1.84	12.2	14.1	3.62
19	3.71	18.06	1.58	1.72	14.6	14.6	4.30
23	3.45	21.51	1.89	1.65	15.8	14.7	2.09
27	2.57	24.08	2.11	1.53	20.0	15.3	2.28
31	2.98	27.06	2.37	1.53	17.4	–	–
35	2.76	29.82	2.62	1.60	20.7	–	–
39	2.88	32.70	2.87	1.63	18.8	–	–

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[*] 11.4 kg waste per experiment.

TABLE A–II

RESULTS OF LABORATORY WEATHERING EXPERIMENTS USING HIGH–SULFUR COAL PREPARATION WASTE TREATED WITH 0.33% LIME

Time (Weeks)	Volume (ℓ)	Cum Volume (ℓ)	Cum Vol[*]/ Mass Waste (cm^3/g)	pH	Cond (mmho/cm)	Total Fe (mg/cm^3)	Fe (II) (mg/cm^3)
3	0.50	0.50	0.044	2.47	5.10	1.66	0.67
4	0.65	1.15	0.101	2.19	7.50	4.29	1.65
5	0.91	2.05	0.180	2.19	7.75	4.72	2.03
6	0.86	2.92	0.256	2.21	8.75	10.1	3.30
7	1.04	3.96	0.347	2.23	11.8	10.4	3.12
8	1.02	4.98	0.437	2.22	11.6	11.3	2.90
9	1.01	5.99	0.525	1.99	12.0	13.0	3.85
10	0.83	6.82	0.598	1.77	18.5	22.1	7.87
11	1.10	7.92	0.695	1.99	11.0	14.3	4.75
12	1.06	8.98	0.788	1.86	12.5	10.3	2.93
13	0.86	9.84	0.863	1.82	15.3	11.8	4.45
15	4.12	13.96	1.22	1.85	12.2	10.0	3.30
19	3.89	17.85	1.57	1.76	13.4	16.2	3.71
23	3.59	21.44	1.88	1.71	14.5	15.0	2.01
27	2.87	24.31	2.13	1.59	18.5	19.9	3.07
31	3.26	27.57	2.42	1.58	15.5	–	–
35	3.03	30.60	2.68	1.64	16.1	–	–
39	3.21	33.81	2.97	1.61	17.6	–	–

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[*] 11.4 kg waste per experiment.

TABLE A–III

RESULTS OF LABORATORY WEATHERING EXPERIMENTS USING HIGH–SULFUR COAL PREPARATION WASTE TREATED WITH 0.53% LIME

Time (Weeks)	Volume (ℓ)	Cum Volume (ℓ)	Cum Vol[a]/ Mass Waste (cm^3/g)	pH	Cond (mmho/cm)	Total Fe (mg/cm^3)	Fe (II) (mg/cm^3)
3	0.75	0.75	0.066	3.80	2.05	0.004	0.002
4	0.65	1.40	0.123	2.75	2.85	0.121	0.010
5	0.82	2.22	0.195	2.56	4.00	1.34	0.610
6	0.77	2.99	0.262	2.38	6.70	3.55	1.42
7	0.73	3.72	0.326	2.25	11.3	6.97	3.52
8	0.89	4.61	0.404	2.29	12.0	13.1	2.90
9	0.95	5.56	0.488	2.02	12.6	14.5	3.94
10	0.81	6.37	0.559	1.88	175	21.9	7.79
11	1.11	7.48	0.656	2.02	11.7	18.9	3.56
12	1.05	8.53	0.748	1.87	13.5	22.9	4.02
13	0.94	9.47	0.831	1.81	16.0	18.3	5.35
15	4.12	13.59	1.19	1.79	14.0	20.0	3.66
19	3.85	17.44	1.53	1.63	17.0	15.7	2.85
23	3.52	20.96	1.84	1.54	19.3	22.7	2.28
27	2.87	23.83	2.09	1.43	23.0	21.6	3.15
31	3.07	26.90	2.36	1.49	20.0	–	–
35	2.82	29.72	2.61	1.52	17.9	–	–
39	2.96	32.68	2.87	1.49	22.0	–	–

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[a] 11.4 kg waste per experiment.

TABLE A–IV

RESULTS OF LABORATORY WEATHERING EXPERIMENTS USING HIGH–SULFUR COAL PREPARATION WASTE TREATED WITH 1.1% LIME

Time (Weeks)	Volume (ℓ)	Cum Volume (ℓ)	Cum Vol[a]/ Mass Waste (cm^3/g)	pH	Cond (mmho/cm)	Total Fe (mg/cm^3)	Fe (II) (mg/cm^3)
3	0.60	0.60	0.053	2.22	7.70	0.001	0.001
4	0.60	1.20	0.105	3.76	3.15	0.001	0.001
5	0.82	2.02	0.177	3.41	2.16	0.006	0.006
6	0.84	2.86	0.251	4.15	2.05	0.001	0.000
7	0.72	3.58	0.314	3.71	2.15	0.001	0.000
8	0.80	4.38	0.384	3.65	2.30	0.001	0.000
9	0.69	5.07	0.445	3.01	2.50	0.004	0.001
10	0.51	5.58	0.489	2.92	2.85	0.003	0.001
11	0.97	6.55	0.574	3.04	3.05	0.030	0.006
12	0.80	7.35	0.645	2.82	3.29	0.029	0.004
13	0.58	7.93	0.696	2.55	6.40	1.22	0.469
15	3.26	11.19	0.982	2.37	5.50	–	–
19	3.03	14.22	1.25	2.07	11.0	14.4	2.76
23	3.35	17.57	1.54	1.97	13.1	22.7	2.09
27	2.64	20.21	1.77	1.76	17.3	29.1	4.32
31	3.10	23.31	2.04	1.61	16.2	–	–
35	2.80	26.11	2.29	1.59	18.5	–	–
39	2.85	28.96	2.54	1.51	20.5	–	–

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[a] 11.4 kg waste per experiment.

TABLE A–V

RESULTS OF LABORATORY WEATHERING EXPERIMENTS USING HIGH–SULFUR COAL PREPARATION WASTE TREATED WITH 3.3% LIME

Time (Weeks)	Volume (ℓ)	Cum Volume (ℓ)	Cum Vol*/ Mass Waste (cm³/g)	pH	Cond (mmho/cm)	Total Fe (mg/cm³)	Fe (II) (mg/cm³)
3	0.40	0.40	0.035	11.70	4.20	0.000	0.000
4	0.50	0.90	0.079	11.60	3.00	0.000	0.000
5	0.70	1.60	0.140	11.47	2.57	0.000	0.000
6	0.59	2.19	0.192	11.27	2.58	0.000	0.000
7	0.60	2.79	0.245	11.09	2.45	0.000	0.000
8	0.70	3.49	0.306	10.76	–	0.000	0.000
9	0.68	4.17	0.366	9.3	2.38	0.000	0.000
10	0.46	4.63	0.406	8.0	2.55	0.000	0.000
11	0.88	5.51	0.483	7.3	2.53	0.000	0.000
12	0.73	6.24	0.547	7.1	2.50	0.001	0.000
13	0.60	6.84	0.600	7.1	2.32	0.001	0.001
15	2.88	9.72	0.853	4.8	2.89	0.002	0.001
19	2.19	11.91	1.04	4.6	2.51	0.002	0.000
23	1.20	13.11	1.15	3.6	2.45	0.003	0.000
27	0.60	13.71	1.20	3.6	2.50	0.004	0.000
31	0.51	14.22	1.25	3.6	2.65	–	–
35	0.43	14.65	1.28	3.04	3.30	–	–
39	0.04	14.69	1.29	2.52	5.00	–	–

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*11.4 kg waste per experiment.

TABLE A–VI

RESULTS OF LABORATORY WEATHERING EXPERIMENTS USING HIGH–SULFUR COAL PREPARATION WASTE TREATED WITH 0.35% LIME AND 1.1% LIMESTONE

Time (Weeks)	Volume (ℓ)	Cum Volume (ℓ)	Cum Vol*/ Mass Waste (cm³/g)	pH	Cond (mmho/cm)	Total Fe (mg/cm³)	Fe (II) (mg/cm³)
3	0.50	0.50	0.055	7.35	2.20	0.000	0.000
4	0.60	1.10	0.121	7.34	2.20	0.000	0.000
5	0.77	1.87	0.205	7.34	1.93	0.001	0.000
6	0.73	2.60	0.286	7.40	2.02	0.000	0.000
7	0.67	3.27	0.359	7.63	2.01	0.000	0.000
8	0.96	4.23	0.465	7.31	2.00	0.000	0.000
9	0.72	4.95	0.544	7.54	1.85	0.000	0.000
10	0.63	5.58	0.613	7.51	2.08	0.000	0.000
11	0.99	6.57	0.722	7.53	1.82	0.000	0.000
12	0.83	7.40	0.813	7.43	1.82	0.000	0.000
13	0.59	7.99	0.878	7.68	2.00	0.000	0.000
15	3.36	11.35	1.25	7.49	1.80	–	0.000
19	2.41	13.76	1.51	4.44	2.40	0.011	0.002
23	1.97	15.73	1.73	2.35	7.11	4.19	0.283
27	2.08	17.81	1.96	1.90	15.0	10.9	4.51
31	3.12	20.93	2.30	1.66	–	–	–
35	3.09	24.02	2.64	1.70	16.0	–	–
39	2.94	26.96	2.96	1.56	19.0	–	–

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*9.1 kg waste per experiment.

TABLE A–VII

TRACE ELEMENT CONCENTRATIONS IN THE LEACHATES FROM TREATED HIGH–SULFUR COAL PREPARATION WASTES

Experiment ID	Time (Weeks)	pH	Ni (ppm)	Al (ppm)	Mn (ppm)	Cu (ppm)	Zn (ppm)	Co (ppm)	Ca (ppm)	K (ppm)	Na (ppm)	Cd (ppm)
No. 1; 0.17% CaO	3	2.37	26	190	53	1.2	18.4	7.9	510	190	<6	<1
No. 1; 0.17% CaO	5	2.16	28	270	57	2.2	13.6	9.4	460	220	<10	<2
No. 1; 0.17% CaO	10	1.73	60	460	72	12.9	<3	19.2	820	340	<30	<5
No. 1; 0.17% CaO	15	1.84	51	370	41	4.3	<3	6.4	610	380	<30	<5
No. 1; 0.17% CaO	27	1.53	45	420	32	3.7	<3	<4	720	260	<30	<5
No. 1; 0.17% CaO	39	1.63	45	410	21	<3	<3	<4	710	160	<30	<5
No. 2; 0.33% CaO	3	2.47	14	97	39	1.4	13	5.6	490	94	<2	<0.3
No. 2; 0.33% CaO	5	2.19	25	120	55	2.9	19.7	7.6	490	151	<6	<1
No. 2; 0.33% CaO	10	1.77	53	450	70	6.6	<3	7.8	830	196	<30	<5
No. 2; 0.33% CaO	15	1.85	34	330	43	3.4	<3	<4	620	<200	<30	<5
No. 2; 0.33% CaO	27	1.59	33	390	31	3.6	<3	5.5	700	<200	<30	<5
No. 2; 0.33% CaO	39	1.61	45	390	22	5.0	<3	<4	700	<200	<30	<5
No. 3; 0.53% CaO	3	3.80	2.3	3.4	7.9	0.03	1.15	0.6	440	40	7.9	<0.03
No. 3; 0.53% CaO	4	2.75	4.4	18.1	14.1	0.18	4.0	1.9	390	48	8.2	<0.03
No. 3; 0.53% CaO	5	2.58	9.5	58	28	0.56	9.7	3.9	430	75	<2	<0.3
No. 3; 0.53% CaO	12	1.87	22	340	56	8.6	<3	11.6	780	250	<30	<5
No. 3; 0.53% CaO	15	1.79	30	380	52	6.1	4.6	5.0	780	177	<30	<5
No. 3; 0.53% CaO	27	1.43	27	380	36	<3	<3	7.4	820	300	<30	<5
No. 3; 0.53% CaO	39	1.49	15	370	21	<3	<3	6.4	790	<200	<30	<5
No. 4; 1.12% CaO	3	2.2	0.18	2.9	0.17	0.03	<0.02	0.03	1480	71	19.2	<0.03
No. 4; 1.12% CaO	10	2.92	1.64	10.2	5.8	0.06	1.54	0.64	400	57	10.6	<0.03
No. 4; 1.12% CaO	12	2.81	3.1	18.7	10.0	0.30	3.3	1.2	450	37	7.4	<0.03
No. 4; 1.12% CaO	15	2.37	11.6	97	27	1.3	10.1	3.3	410	93	<2	<0.3
No. 4; 1.12% CaO	19	2.08	50	460	62	<3	8.4	5.0	920	420	<30	<5
No. 4; 1.12% CaO	27	1.76	50	460	70	5.4	<3	8.8	900	<200	<30	<5
No. 4; 1.12% CaO	39	1.51	29	420	37	<3	<3	<4	830	<200	<30	<5
No. 5; 3.3% CaO	3	11.7	0.36	1.11	0.04	<0.02	<0.02	<0.03	700	25	7.7	<0.04
No. 5; 3.3% CaO	15	4.77	0.34	1.35	0.06	<0.02	<0.02	<0.03	520	29	5.0	<0.03
No. 5; 3.3% CaO	23	3.61	0.19	1.63	0.13	<0.02	0.02	<0.03	470	26	3.7	<0.03
No. 5; 3.3% CaO	39	2.52	4.1	62	16.13	1.3	4.5	1.4	510	44	6.0	<0.04
No. 6; 0.35% CaO 1.1% CaCO$_3$	3	7.35	0.37	1.35	1.55	<0.02	<0.02	<0.03	470	28	5.2	<0.04
No. 6; 0.35% CaO 1.1% CaCO$_3$	15	7.49	0.40	1.21	1.62	0.03	<0.02	0.08	380	17	1.05	<0.03
No. 6; 0.35% CaO 1.1% CaCO$_3$	19	4.44	6.4	31	19.8	0.66	5.6	2.8	410	26	1.63	<0.03
No. 6; 0.35% CaO 1.1% CaCO$_3$	23	2.35	33	210	51	<1	9.4	8.6	560	<50	<10	<2
No. 6; 0.35% CaO 1.1% CaCO$_3$	27	1.90	57	400	85	5.2	18.1	12.6	770	<100	<20	<3
No. 6; 0.35% CaO 1.1% CaCO$_3$	31	1.66	65	420	75	<3	<3	12.6	860	<200	<30	<5
No. 6; 0.35% CaO 1.1% CaCO$_3$	39	1.56	56	390	46	<3	<3	<4	850	<200	<30	<5
H$_2$O. Control			0.05	<0.3	0.01	<0.02	<0.02	<0.02	2.3	<0.9	<0.2	<0.02

TABLE A–VIII

DISCHARGE SEVERITIES FOR TRACE ELEMENTS IN THE LEACHATES FROM TREATED HIGH–SULFUR COAL PREPARATION WASTES

Experiment ID	Time (Weeks)	pH	Fe	Ni	Al	Mn	Cu	Zn	Co	Ca	K	Cd
No. 1; 0.17% CaO	3	2.37	150	26.0	1.90	5.30	0.240	1.84	0.316	0.319	0.044	<10
No. 1; 0.17% CaO	5	2.16	339	28.0	2.70	5.70	0.440	1.36	0.375	0.288	0.051	<20
No. 1; 0.17% CaO	10	1.73	856	60.0	4.60	7.20	2.58	<2.300	0.768	0.512	0.079	<50
No. 1; 0.17% CaO	15	1.84	564	51.0	3.70	4.10	0.860	<0.300	0.256	0.381	0.088	<50
No. 1; 0.17% CaO	27	1.53	612	45.0	4.20	3.20	0.740	<0.300	<0.160	0.450	0.060	<50
No. 2; 0.33% CaO	3	2.47	66.4	14.0	0.97	3.90	0.280	1.30	0.224	0.306	0.022	<3
No. 2; 0.33% CaO	5	2.19	189	25.0	2.20	5.50	0.580	1.97	0.304	0.306	0.035	<10
No. 2; 0.33% CaO	10	1.77	884	53.0	4.50	7.00	1.32	<0.300	0.312	0.519	0.046	<50
No. 2; 0.33% CaO	15	1.85	400	34.0	3.30	4.30	0.680	<0.300	<0.160	0.388	<0.046	<50
No. 2; 0.33% CaO	27	1.59	796	33.0	3.90	3.10	0.720	<0.300	0.220	0.438	<0.046	<50
No. 2; 0.33% CaO	39	1.61	–	45.0	3.90	2.20	1.00	<0.300	<0.160	0.438	<0.046	<50
No. 3; 0.53% CaO	3	3.80	0.156	2.30	0.034	0.79	0.006	0.115	0.024	0.275	0.009	<0.3
No. 3; 0.53% CaO	4	2.75	4.84	4.40	0.181	1.41	0.036	0.400	0.076	0.244	0.011	<0.3
No. 3; 0.53% CaO	5	2.58	53.6	9.50	0.580	2.80	0.112	0.970	0.156	0.269	0.017	<3
No. 3; 0.53% CaO	12	1.87	916	22.0	3.40	5.60	1.72	<0.300	0.464	0.488	0.058	<50
No. 3; 0.53% CaO	15	1.79	800	30.0	3.80	5.20	1.22	0.460	0.200	0.488	0.041	<50
No. 3; 0.53% CaO	27	1.43	864	27.0	3.80	3.60	<0.600	<0.300	0.296	0.512	0.070	<50
No. 3; 0.53% CaO	39	1.49	–	15.0	3.70	2.10	<0.600	<0.300	0.256	0.494	<0.046	<50
No. 4; 1.12% CaO	3	2.22	0.056	0.180	0.029	0.017	0.006	<0.002	0.001	0.925	0.016	<0.3
No. 4; 1.12% CaO	10	2.92	0.103	1.64	0.102	0.980	0.012	0.154	0.026	0.250	0.013	<0.3
No. 4; 1.12% CaO	12	2.81	1.16	3.10	0.187	1.00	0.060	0.330	0.048	0.281	0.009	<0.3
No. 4; 1.12% CaO	15	2.37	–	11.6	0.970	2.70	0.260	1.01	0.132	0.256	0.022	<3
No. 4; 1.12% CaO	19	2.08	576	50.0	4.60	6.20	<0.600	0.840	0.200	0.575	0.098	<50
No. 4; 1.12% CaO	27	1.76	1160	70.0	4.60	7.00	1.080	<0.300	0.352	0.562	<0.046	<50
No. 4; 1.12% CaO	39	1.51	–	29.0	4.20	3.70	<0.600	<0.300	<0.160	0.519	<0.046	<50
No. 5; 3.3% CaO	3	11.7	0.011	0.360	0.0111	0.004	<0.004	<0.002	<0.001	0.438	0.006	<0.4
No. 5; 3.3% CaO	15	4.77	0.075	0.340	0.0135	0.006	<0.004	<0.002	<0.001	0.325	0.007	<0.3
No. 5; 3.3% CaO	23	3.61	0.120	0.190	0.0163	0.013	<0.004	0.002	<0.001	0.294	0.006	<0.3
No. 5; 3.3% CaO	39	2.52	–	4.10	0.620	1.613	0.260	0.450	0.056	0.319	0.010	<0.4
No. 6; 0.35% CaO 1.1% $CaCO_3$	3	7.35	0.0004	0.370	0.0135	0.155	<0.004	<0.002	<0.001	0.294	0.006	<0.4
No. 6; 0.35% CaO 1.1% $CaCO_3$	15	7.49	–	0.400	0.0121	0.162	0.066	<0.002	0.003	0.238	0.004	<0.3
No. 6; 0.35% CaO 1.1% $CaCO_3$	19	4.44	0.432	6.40	0.310	1.98	0.132	0.560	0.112	0.256	0.006	<0.3
No. 6; 0.35% CaO 1.1% $CaCO_3$	21	3.05	–	14.8	1.00	4.10	0.360	1.36	0.252	0.256	0.010	<0.7
No. 6; 0.35% CaO 1.1% $CaCO_3$	23	2.35	168	33	2.10	5.10	<0.200	0.940	0.344	0.350	<0.012	<20
No. 6; 0.35% CaO 1.1% $CaCO_3$	27	1.90	436	57	4.00	8.50	1.04	1.81	0.504	0.481	<0.023	<30
No. 6; 0.35% CaO 1.1% $CaCO_3$	31	1.66	–	65.0	4.20	7.50	<0.600	<0.300	0.504	0.538	<0.046	<50
No. 6; 0.35% CaO 1.1% $CaCO_3$	39	1.56	–	56.0	3.90	4.60	<0.600	<0.300	<0.160	0.531	<0.046	<50

barrel each) were placed in molded plastic pans previously fitted with Tygon drains, then covered with glass wool and a layer of sand. The pans were then placed in a 6-column by 6-row grid for weathering by wet and dry cycles.

The weathering cycles consisted of weekly "rain showers" of 1650 mℓ deionized water (equivalent to 39 in./yr), with the drains stoppered. The following day the drains were opened and the leachates collected. The pH, specific conductance, volume, and ferric and ferrous ion concentrations were measured weekly and the trace element concentrations were determined later. The drained boxes of lime/limestone/waste were allowed to dry until the following week and the cycle was started again.

APPENDIX B

PROCEDURES AND RESULTS FOR EXPERIMENTS ON CODISPOSAL OF COAL WASTES WITH SOILS OR PROCESS WASTES

I. EXPERIMENT A. ATTENUATION OF ACIDITY AND TRACE ELEMENTS BY A CALCAREOUS MINE OVERBURDEN

This experiment was designed to investigate three possible treatments for *in situ* attenuation of acidity and trace elements with mine overburden from Kentucky coal seam 11. Seam 11 overburden has a moderate amount of carbonaceous minerals and cation exchange capacity as shown in Tables I (main body of the report) and B-I, and therefore, is reasonably typical of material found at many active mining locations.

The three disposal treatments were described by the experimental procedure in the main body of this report (Sec. I.A.2.a).

Treatment columns 1 and 2 had –3/8-in. soil mixed with coal waste because we felt that this material was the most practical size for field applications of codisposal of

TABLE B-I

MINERALOGY OF SUBSOILS AND QUARRY LIMESTONE USED IN ATTENUATION AND CODISPOSAL EXPERIMENTS

	Quartz	Calcite	Illite	Kaolinite	Montmorillonite	Mixed Layer Clays
Seam 11 overburden	33.0	3.6	22.2	7.8	2.2	0.0
Seam 12 overburden	55.6	0.6	22.2	9.9	0.0	0.0
Acid Loess subsoil (OKAW)	48.2	0.0	5.1	0.7	0.0	12.3
Calcareous Till subsoil (BS3)	39.4	6.5	7.3	1.2	0.0	17.4
Quarry[a] limestone (Ill.)	4.1	70.0	—	—	—	—

overburden and waste. Treatment 1 tested the effectiveness of codisposing coal cleaning waste and a mine overburden by conventional tillage procedures with no additional control measures. Treatment 2 simply added the control of a semipermeable soil liner below the waste to take advantage of a calcareous soil's natural capability for neutralizing and sorbing contaminants. Treatment 3 uses only the soil liner, although much more of it than treatment 2.

The columns were leached with distilled water for 21 days at 10 mℓ/h until about 5 ℓ had passed through. Direction of flow was upward. Column, influent water, and effluent leachate were maintained under an argon atmosphere throughout leaching to retard pyrite oxidation and conversion of Fe(II) to Fe(III). Eh, pH, specific conductance, Fe(II), and total dissolved Fe were monitored throughout. After cessation of leaching, columns were dried and water-saturated air was forced through them for 2 weeks to promote pyrite oxidation in an attempt to regenerate acidity and high trace element levels. This was done to test the efficacy of the soil treatment at retarding pyrite oxidation. After the oxidation procedure, each column was leached again with about 1 ℓ of deionized (Milli-Q) water and analyzed as above. Selected aliquots were also analyzed for fluorine, aluminum, manganese, nickel, and arsenic. This subset of elements was selected as indicative of general trace element behavior. Raw data from these experiments, listed in Tables B-II through B-V, show that none of the treatments completely controlled contaminants from this coal cleaning waste.

II. EXPERIMENT B. CODISPOSAL OF COAL CLEANING WASTE AND FINELY GROUND SUBSOILS

This experiment was a follow-up to treatment 1, which indicated that codisposal of −3/8-in. soil with coal cleaning waste was unsatisfactory for mitigating the water pollution potential of the waste.

In this experiment, finely ground soils were mixed with −3/8-in. coal cleaning waste to test the efficacy of codisposing soils and wastes under near optimal conditions. If effective, ways to attain such mixtures in the field could be investigated. Earlier experiments showed that limestone ($CaCO_3$) is more effective at neutralizing acidic waste leachates when present as smaller particles.

Materials used in this experiment and some of their properties are shown in Tables I (main body of the report) and B-I. These materials were collected at or near active coal mining sites in the Illinois Basin.

TABLE B-II

RESULTS FOR TREATMENT 1 OF EXPERIMENT ON ATTENUATION OF ACIDITY AND TRACE ELEMENT CONCENTRATIONS BY MINE OVERBURDEN

	Sample					
	1	6	12	19	33	35-36
Vol (ℓ)	0.195	0.5	0.993	2.39	4.49	4.89
pH	2.6	3.29	4.74	6.48	6.50	2.0
Cond (μmho)	13 200	7 000	2 800	2 300	1 300	7 600
Fe(II)	6 166	3 857	1 190	160	23	3 801
Fe(III)	1 257	165	15	2.0	<0.02	7 349
F	15.3	7.6	2.4	<0.5	<0.5	38.2
Al	870	105	2.7	0.06	0.05	406
Mn	116.4	57.9	24	5.1	1.5	99
Ni	25	13	4	0.4	<0.02	9.6
As	2.2	0.09	0.014	<0.001	<0.001	2.8

TABLE B-III

RESULTS FOR TREATMENT 2 OF EXPERIMENT ON ATTENUATION OF ACIDITY AND TRACE ELEMENT CONCENTRATIONS BY MINE OVERBURDEN

	Sample					
	1	6	12	18	34	35-38
Vol (ℓ)	0.094	0.526	0.956	2.378	4.411	5.87
pH	4.4	6.14	6.39	6.35	6.80	2.33
Cond (μmho)	8 300	3 400	2 800	3 100	1 600	7 600
Fe(II)	3 396	1 236	652	435	48	1 900
Fe(III)	700	68	6.0	<0.02	<0.02	6 498
F	4	1.6	<0.5	<0.5	<0.5	31.7
Al	52.9	0.6	0.05	0.06	<0.04	343
Mn	140	25.7	15.8	11.4	2.3	79
Ni	19	4	2.1	1.1	0.1	7.5
As	0.033	0.020	<0.002	<0.001	<0.001	3.7

TABLE B-IV

RESULTS FOR TREATMENT 3 OF EXPERIMENT ON ATTENUATION OF ACIDITY AND TRACE ELEMENT CONCENTRATIONS BY MINE OVERBURDEN

	Sample					
	1	5	11	20	36	38-41
Vol (ℓ)	0.140	0.486	0.976	2.557	4.934	5.40
pH	4.6	5.0	6.4	6.7	7.0	2.5
Cond (μmho)	9 600	5 900	2 800	2 250	1 100	5 400
Fe(II)	5 895	3 097	997	65	17	1 384
Fe(III)	305	341	19	1	<0.02	6 782
F	8	2.7	<0.5	<0.5	0.6	22.5
Al	45.4	9.1	<0.04	<0.08	<0.04	331
Mn	101	35	10.4	2.1	0.7	37
Ni	23	8	1.5	0.05	<0.02	5.4
As	<0.005	<0.001	<0.001	<0.001	<0.001	0.9

TABLE B-V

RESULTS FOR TREATMENT 4 OF EXPERIMENT ON ATTENUATION OF ACIDITY AND TRACE ELEMENT CONCENTRATIONS BY MINE OVERBURDEN

	Sample					
	1	6	12	19	35	36-38
Vol (ℓ)	0.093	0.450	0.958	2.3	4.78	5.24
pH	1.40	1.67	2.10	2.80	3.45	1.59
Cond (μmho)	34 000	13 950	3 600	640	300	15 700
Fe(II)	12 876	4 754	690	33	10	4 696
Fe(III)	3 473	234	<0.02	<0.02	<0.02	3 123
F	19.4	11.9	3.5	<0.5	<0.05	5.9
Al	793	210	22.4	0.4	0.2	142
Mn	36.7	9.5	2.1	0.05	0.04	7.5
Ni	33	9.0	1.5	0.04	<0.02	3.5
As	2.2	0.85	0.32	0.14	0.09	2.5

Six glass columns, 6-cm i.d. by 38 cm long, were filled with these soils as follows:

Column	(g)	Mixture	(g)
1A,1B	240	Ky. Seam 11,	360 waste
2	384	Ky. Seam 12,	216 waste
3	506	Acidic Loess,	94 waste
4	160	Calcareous Till,	440 waste
5	48	Quarry Limestone,	552 waste
6			365 waste

The quantity of soil or overburden used was based on providing enough titratable carbonate to neutralize 150% of the leachable waste acidity. Waste acidity was determined by titration after extraction of the waste with an H_2O_2 solution (ASTM Method D 1067E). Column 1 was duplicated and 1B was maintained under an air atmosphere to determine whether air had any effect on the results. All other columns were maintained under argon to prevent oxidation of Fe(II) to Fe(III).

About 4 ℓ of deionized water was passed through each column (upward flow) at a rate of 4-6 mℓ/h. Then the soil-waste mixtures were extruded from the columns, allowed to air-oxidize for several days, and batch-leached using a 5:1 water-to-solid mass ratio. Column influent, effluent, and batch leachates were monitored for pH, specific conductance, total dissolved Fe, Fe(II), Al, As, F, Mn, and Ni. Ferric iron was determined by the difference between total iron and ferrous iron. Iron, pH, and conductance measurements were performed on virtually all samples. The remaining parameters were determined from aliquots selected by pH and iron results to obtain sufficient data points for definition of contaminant concentration versus volume profiles. These results are completely listed in Tables B-VI through B-XII and are discussed in Sec. I.A.2.b. in the main text.

TABLE B-VI

VALUES OF MEASURED PARAMETERS AT VARIOUS EFFLUENT VOLUMES FOR EXPERIMENTS ON CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS—CONTROL

Cumulative Volume (ℓ)	pH	Conductivity (μmho)	Fe^{2} mg/ℓ	Fe^{tot} mg/ℓ	F mg/ℓ	Al mg/ℓ	Mn mg/ℓ	Ni mg/ℓ	As mg/ℓ
0.142	1.9	17000	6600	8510					
0.306	1.9	11000	4750	5730	14	570	2.4	7.7	1.68
0.676	2.4	7700	1930	2170					
1.026	2.4	5400	880	1010	1.0	62	2.3	1.91	0.19
1.308	2.4	4100	850	880					
1.633	2.4	3700	770	830					
1.739	2.5	3200	870	880					
1.881	2.4	3700	790	860					
2.251	2.4	3100	610	660					
2.389	2.6	2600	540	600					
2.614	2.5	2450	340	480	0.61	32	1.3	1.06	0.13
3.269	2.7	2150	560	690					
3.391	2.7	1500	370	440	0.7	26	1.2	0.89	0.078
3.577	2.6		280	320					
3.826	2.7	1000	200	260	0.27	10.8	0.6	0.45	0.078
REG	2.3		640	1100	0.68	44.4	1.4	1.08	0.144

TABLE B-VII

VALUES OF MEASURED PARAMETERS AT VARIOUS EFFLUENT VOLUMES FOR EXPERIMENTS ON CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS—SEAM 11 OVERBURDEN (AIR)

Cumulative Volume (mℓ)	pH	Conductivity (μmho)	Fe^{2} (mg/ℓ)	Fe^{tot} (mg/ℓ)	F (mg/ℓ)	Al (mg/ℓ)	Mn (mg/ℓ)	Ni (mg/ℓ)	As (mg/ℓ)
0.158	4.1	7500	3980	4200	0.4	5.9	82	17.8	0.014
0.268	4.9	5400	2180	2430					
0.448	4.1	3500	1516	1620					
0.878	4.9	2800	810	800					
1.258	5.5	2600	320	380	<0.02	<0.02	17	0.46	<0.001
1.595	5.8	2300	140	140					
1.955	6.9	2200	2	27	<0.2	<0.2	5.7	<0.01	<0.001
2.075	7.7	1950	1	4					
2.238	7.6	2150	0.22	1.9	<0.2	<0.2	3.3	<0.01	<0.001
2.638	7.7	2300	0.05	0.7					
2.808	7.8	2100	0.05	0.3					
3.088	8.0	2100	0.03	<0.02	<0.2	<0.2	1.6	<0.01	<0.001
3.250	8.0	2050	<0.02	<0.02					
3.420	8.0	2050	<0.02	<0.02					
3.670	8.1	2100	<0.02	<0.02	<0.2	<0.2	5.0	<0.01	<0.001
REG	2.9		200	240	2.9	33.5	20.7	2.53	0.007

TABLE B-VIII

VALUES OF MEASURED PARAMETERS AT VARIOUS EFFLUENT VOLUMES FOR EXPERIMENTS ON CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS—SEAM 11 OVERBURDEN (ARGON)

Cumulative Volume (ℓ)	pH	Conductivity (μmho)	Fe^{2} (mg/ℓ)	Fe^{tot} (mg/ℓ)	F (mg/ℓ)	Al (mg/ℓ)	Mn (mg/ℓ)	Ni (mg/ℓ)	As (mg/ℓ)
0.142	4.8	9000	6570	6964	0.21	1.5	55	23.7	0.02
0.266	4.9	5700	2416	2577					
0.448	4.3	4800	1413	1549					
0.888	6.4	3100	543	594	<0.2	<0.2	21	1.55	0.002
1.328	6.2	2200	106	127					
1.708	6.7	2100	49	56	<0.2	<0.2	5.2	0.02	<0.001
2.108	7.7	2250	3	22	<0.2	<0.2	2.7	<0.01	<0.001
2.238	8.1	1950	0.4	2					
2.418	8.1	2000	0.7	2					
2.888	7.7	2250	0.9	3					
3.081	7.8	2100	0.8	2	<0.2	<0.2	0.9	<0.01	<0.001
3.371	7.9	2000	1.4	1.5					
3.565	7.8	2000	<0.02	<0.02					
3.775	7.9				<0.2	<0.1		<0.01	<0.001
4.075	8.0	2000	<0.02	<0.02					
REG	3.0		156	188	2.6	27.8	18.7	2.01	0.004

TABLE B-IX

VALUES OF MEASURED PARAMETERS AT VARIOUS EFFLUENT VOLUMES FOR EXPERIMENTS ON CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS—SEAM 12 OVERBURDEN

Cumulative Volume (ℓ)	pH	Conductivity (μmho)	Fe^{2} (mg/ℓ)	Fe^{tot} (mg/ℓ)	F (mg/ℓ)	Al (mg/ℓ)	Mn (mg/ℓ)	Ni (mg/ℓ)	As (mg/ℓ)
0.188	4.0	8800	4620	5140	6.3	130	78	16.3	0.019
0.316	4.3	6500	3490	3770					
0.511	4.0	5400	2560	2740					
0.941	5.2	3200	820	910					
1.356	5.2	2900	310	360	<0.2	<0.2	9.1	1.1	0.002
1.685	6.0	2200	170	180					
2.053	5.4	1600	71	74	<0.2	<0.2	3.6	0.26	0.001
2.173	5.9	1600	61	63					
2.343	6.0	1775	39	41					
2.793	6.5	1500	18	18					
2.961	6.8	1200	8	9					
3.251	7.4	1275	<0.02	<0.02	<0.2	<0.2	1.4	0.02	<0.001
3.441	7.4	880	<0.02	<0.02					
3.641	7.2		<0.02	<0.02					
3.931			<0.02	<0.02	<0.2	<0.2	1.0	0.03	<0.001
REG	2.8		150	190	1.6	16.1	6.4	0.47	0.005

TABLE B-X

VALUES OF MEASURED PARAMETERS AT VARIOUS EFFLUENT VOLUMES FOR EXPERIMENTS ON CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS—ACID LOESS SUBSOIL (OKAW)

Cumulative Volume (ℓ)	pH	Conductivity (μmho)	Fe^{2} (mg/ℓ)	Fe^{tot} (mg/ℓ)	F (mg/ℓ)	Al (mg/ℓ)	Mn (mg/ℓ)	Ni (mg/ℓ)	As (mg/ℓ)
0.123	3.6	2400	310	370	1.4	23.1	80	1.62	0.008
0.247	3.8	1850	230	250					
0.597	3.7	1240	62	80					
1.067	3.6	960	81	80					
1.442	3.7	980	62	77	0.43	6.6	39	0.67	0.002
1.777	3.7	1300	110	110					
2.237	3.7	840	57	60	0.3	3.9	31	0.47	0.003
2.417	3.8	[illegible]80	60	62					
2.605	3.8	8[illegible]0	52	56					
3.095	3.4	840	48	64					
3.289	3.7	880	46	47					
3.589	3.4	800	18	20	<0.2	1.7	21	0.3	0.003
3.889	3.2	690	23	29					
4.389	3.3		58	73	0.3	2.1	19	0.21	<0.001
REG	3.0		36	48	0.9	11	31	0.5[illegible]	0.004

TABLE B-XI

VALUES OF MEASURED PARAMETERS AT VARIOUS EFFLUENT VOLUMES FOR EXPERIMENTS ON CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS—CALCAREOUS TILL SUBSOIL (BS#3)

Cumulative Volume (ℓ)	pH	Conductivity (μmho)	Fe^{2} (mg/ℓ)	Fe^{tot} (mg/ℓ)	F (mg/ℓ)	Al (mg/ℓ)	Mn (mg/ℓ)	Ni (mg/ℓ)	As (mg/ℓ)
0.134	5.1	6300	3120	3300	<0.2	0.2	200	8.3	0.002
0.444	4.3	4400	2510	2680		<0.2			
0.884	6.3	2700	680	740					
1.234	5.8	3000	260	290	<0.2		40	0.55	0.002
1.572	6.4	2300	160	180					
1.987	6.3	1900	24	29					
2.157	6.6	2000	17	20	<0.2	<0.2	12	<0.01	<0.001
2.331	6.8	2200	7	20					
2.781	7.5	2300	2	36					
2.971	7.6	2300	2	21					
3.256	7.8	2300	2	4	<0.2	<0.2	4.4	<0.01	<0.001
3.636	8.0	2200	<0.02	<0.02					
3.916	8.0		<0.02	<0.02	<0.2	<0.2	2.3	<0.01	<0.001
REG	2.4		570	1000	3.3	84	11.3	3.05	0.052

TABLE B-XII

VALUES OF MEASURED PARAMETERS AT VARIOUS EFFLUENT VOLUMES FOR EXPERIMENTS ON CODISPOSAL OF COAL WASTE WITH FINELY GROUND SUBSOILS—QUARRY LIMESTONE

Cumulative Volume (ℓ)	pH	Conductivity (μmho)	Fe^{2} (mg/ℓ)	Fe^{tot} (mg/ℓ)	F (mg/ℓ)	Al (mg/ℓ)	Mn (mg/ℓ)	Ni (mg/ℓ)	As (mg/ℓ)
0.126	4.8	10400	10800	11000	<0.2	1.1	43	21.0	0.004
0.426	4.0	4700	3660	3970	<0.2	<0.2	15	4.6	0.001
0.856	5.2	2600	480	540					
1.206	5.8	2200	95	120					
1.546	6.8	2000	97	100					
1.961	7.3	2200	50	55					
2.131	7.3	1950	5	12	<0.2	<0.2	0.7	<0.01	<0.001
2.301	7.3	2100	3	3					
2.751	7.8	2100	2	6					
2.931	7.8	2100	2	6					
3.221	7.8	2100	3	5					
3.416	8.0	2100	<0.02	<0.02					
3.886	8.0		<0.02	<0.02	<0.2	<0.1	0.2	0.01	<0.001
REG	6.4		4	4	<0.2	0.3	0.8	0.44	0.001

APPENDIX C

TRACE ELEMENT CHEMISTRY OF ACIDIC COAL CLEANING WASTE LEACHATES

by

Lawrence E. Wangen and Joel M. Williams

ABSTRACT

We investigated the chemistry of an acidic leachate from coal cleaning wastes as a function of pH after neutralization with $Ca(OH)_2$. The distribution of the chemical components between solid and liquid forms was determined using a chemical equilibrium model designed for aqueous systems. Major focus is on the use of alkaline neutralization as a technology to control potential contamination by trace elements in acidic coal waste leachates. Results for major components show good agreement between equilibrium model predictions and laboratory measurements. However, predicted concentrations are substantially higher than those measured for most trace elements. Adsorption onto amorphous oxides is suggested as an explanation.

I. INTRODUCTION

Recent research at Los Alamos National Laboratory has shown that, in addition to acid, aluminum, iron, and manganese, many trace inorganic chemical species are present in leachates from the mineral by-products of coal cleaning in excessive concentrations according to water quality criteria.[1] These results led to research aimed at developing methods for reducing leachate concentrations of these elements. In view of the popularity of alkaline neutralization for acidity control in such leachates,[2] its effect on the concentrations of trace species in these waters has been investigated. This report presents results of chemical equilibrium calculations on a coal waste leachate as a function of pH and compares predicted solution concentrations with those obtained by laboratory neutralization of an acidic coal waste leachate with calcium hydroxide. In addition, the speciation of components and controlling solids as predicted by the chemical equilibrium model are presented.

In recent years, several computerized chemical models have been designed to calculate equilibrium concentrations of chemical species in complex aqueous systems.[3] Some models include gas-solution, solid-liquid, complex formation, and oxidation-reduction chemistry, and thus are quite sophisticated in terms of the types and complexity of species modeled. We used a version of MINEQL developed by Morel and Morgan,[4] which contains a fairly extensive data base that includes most of the inorganic species thought to be important in natural water systems. MINEQL uses equilibrium constants at 25°C and 1 bar pressure, the Davies procedure for correction of activity coefficients according to ionic strength,[5] and includes a check for precipitation of any solid species contained in the program's library that could possibly be formed from the list of chemical components input by the user.

II. EXPERIMENTAL PROCEDURE AND CHEMICAL ANALYSES

Table C-I contains a list of components with initial element concentrations in a coal cleaning waste leachate used as input to MINEQL and as starting material for laboratory titrations with $Ca(OH)_2$. A stock coal cleaning waste leachate was obtained by extraction from a quantity of coal waste by deionized water for 30 days at a 5:1 water-to-solid ratio. The resultant slurry was filtered through Whatman 42 filter paper and the filtrate was stored in an argon atmosphere to prevent oxidation of iron from the ferrous to the ferric state. Chemical analyses of the stock leachate throughout several months gave comparable results indicating no appreciable change in major or trace chemical components during storage. Hydrogen ion activity of the stock leachate was 1.0×10^{-2} mole/ℓ (pH = 2.00). The stock leachate was diluted (2 parts leachate with 1 part water) during the lime additions, including the control sample.

TABLE C-I

COMPONENT CONCENTRATIONS AND SPECIATIONS OF LEACHATE FROM A COAL CLEANING WASTE

Component	moles/ℓ	mg/ℓ
Ca(II)	8.73E – 03	3.50E + 02
Mg(II)	2.20E – 03	5.35E + 01
K(I)	4.77E – 04	1.86E + 01
Na(I)	1.45E – 02	3.33E + 02
Fe(III)	2.92E – 02	1.63E + 03
Fe(II)	3.01E – 02	1.68E + 03
Mn(II)	1.80E – 04	9.89E + 00
Cu(II)	1.42E – 06	9.02F – 02
Cd(II)	1.86E – 06	2.09E – 01
Zn(II)	2.45E – 04	1.60E + 01
Ni(II)	1.28E – 04	7.51E + 00
Pb(II)	1.61E – 07	3.34E – 02
Co(II)	5.94E – 05	3.50E + 00
Cr(III)	8.21E – 06	4.27E – 01
Al(III)	1.37E – 0	3.70E + 02
CO_3^{2-}	8.73E – 03	5.24E + 02
SO_4^{2-}	1.23E – 01	1.18E + 04
Cl	2.07E – 04	7.34E + 00
F^-	4.26E – 03	8.09E + 01
PO_4^{3-}	2.46E – 06	2.34E + 00
SiO_3^{2-}	1.78E – 04	1.35E + 01
$B(OH)_4^-$	1.42E – 04	1.12E + 01
MoO_4^{2-}	2.08E – 06	3.33E – 01
AsO_4^{3-}	5.47E – 06	7.60E – 01

Different amounts of hydrated lime $[Ca(0H)_2]$ were added to each of six 250-mℓ, 24/40 opening, Erlenmeyer flasks. Each flask was fitted at the top with a gas entry/exit adapter through which argon flowed at ~7.5 ℓ/min. Each flask was connected in series and contained a stirring bar that was turned from below. Purified

(Milli-Q) water (25 mℓ) was added to each flask and a slurry was made with the lime while stirring 2 h in argon atmosphere. Stock leachate (50 mℓ) was transferred by pipet with argon purging to each flask beginning with the first in the series. After stirring for 24 h and measuring the pH, the contents of each flask were filtered under argon through a 0.45-μm millipore filter. The filtrates were stored in argon in polyethylene bottles. Aliquots were taken to evaluate the Fe(II)/Fe(III) ratios and the remaining filtrates were acidified to 5% concentrated nitric acid for trace element analyses.

Flame or flameless atomic absorption spectrometry was used to analyze most elements; an ion-selective electrode was used to determine F^- ion. Fe(III) was calculated as the difference between total iron and Fe(II), which were determined by the orthophenanthroline procedure. Moles of lime added, equilibrium solution pH, and total solution concentrations of species measured, as well as those predicted by MINEQL, are listed in Table C-II.

Equilibrium Model Calculations

Equilibrium speciations were calculated using MINEQL for all 24 chemical components listed in Table C-I at incremental pH from 1 through 14 and for the specific pH obtained after the $Ca(OH)_2$ additions. From these, total solution concentrations were calculated for comparison with experimental results. (Chemical analyses after $Ca(OH)_2$ additions were performed only for components listed in Table C-II.) Oxidation states and assumed speciation of all initial components are listed in Table C-I. For thermodynamic predictions, multivalent species were set as follows: arsenic as AsO_4^{3-}, chromium as Cr(III), copper as Cu(II), and manganese as Mn(II). These assignments are consistent with a system controlled by the oxidation potential of an Fe(II)-Fe(III) couple. Since the experiments were performed under argon atmosphere to prevent oxidation of Fe(II) to Fe(III), this reaction was not allowed in the thermodynamic calculations. The argon atmosphere also negated the need to consider $CO_2(g)$ exchange with our solutions.

III. RESULTS

A. Comparison of Equilibrium Modeling and Experimental Results for Total Soluble Species

Comparison of measured and predicted total soluble species concentrations after lime additions shows good agreement for F^- and major cations, Ca, Al, Fe(II), and Fe(III), but very poor agreement for trace components, As, Cd, Co, Cr, Cu, Mn, Ni, and Zn. These comparisons are shown in Table C-II and illustrated for Fe(III), AsO_4^{-3}, and Zn(II) in Fig. C-1. Additional comparisons are shown in Fig. C-2a-d.

Total solution concentrations of ferric iron (Fig. C-1) are maintained at low levels by the precipitation of $Fe(OH)_3(s)$ in this system from pH 4-12. In contrast, no

TABLE C–II

MEASURED AND CALCULATED TOTAL SOLUTION CONCENTRATIONS (mg/ℓ)[a]

Lime Added (mmole)[b]	pH	Data Source	Final Element Concentration (mg/ℓ)												
			Ca	Al	FeII	FeIII	AsO_4^{3-}	Cd	Co	Cr	Cu	F	Mn	Ni	Zn
0	2.25	meas.	350	370	1680	1630	0.76	0.21	3.5	0.43	0.09	81	9.9	7.5	16
		Calc.	350	370	1680	1550	0.76	0.21	3.5	0.43	0.09	81	9.9	7.5	16
2.16	2.73	meas.	540	370	1800	160	0.26	0.23	3.7	0.28	0.11	86	10.1	7.7	17
		calc.	393	370	1680	70	0.76	0.21	3.5	0.43	0.09	81	9.9	7.5	16
4.73	5.82	meas.	430	0.46	1350	<0.02	<0.02	0.08	2.8	<0.01	0.01	2.0	10.8	3.8	3
		cal.	447	0.30	1260	0.002	0.76	0.21	3.5	0.43	0.09	4.0	9.9	7.5	16
5.81	6.49	meas.	450	<0.1	620	<0.02	<0.02	<0.03	0.5	<0.01	<0.01	4.2	8.1	0.5	0.5
		calc.	523	0.002	1200.	0.0004	0.76	0.21	3.5	0.13	0.09	3.1	9.9	7.5	11.4
6.76	8.09	meas.	500	<0.1	2.2	<0.02	<0.02	<0.003	<.02	<0.1	<0.01	10	0.3	<0.02	<0.02
		calc.	573	0.001	14.7	1.E-5	0.76	0.21	0.042	0.086	0.09	2.9	8.3	0.15	1.2
8.11	10.18	meas.	490	1.1	<0.02	<0.02	<0.02	<0.009	<0.02	<0.01	<0.01	12	<0.02	<0.02	<0.02
		calc	664	0.17	0.01	0.0006	0.46	0.21	0.04	0.43	0.0003	2.6	0.30	0.0001	0.10

a) speciation used for equilibrium calculations: Ca, Cd, Co, Cu, Mn, Ni, and Zn divalent cations
Al, Cr as trivalent cations
F ; AsO_4^{3-}

b) mmoles added to leachate (final volume 75mℓ)

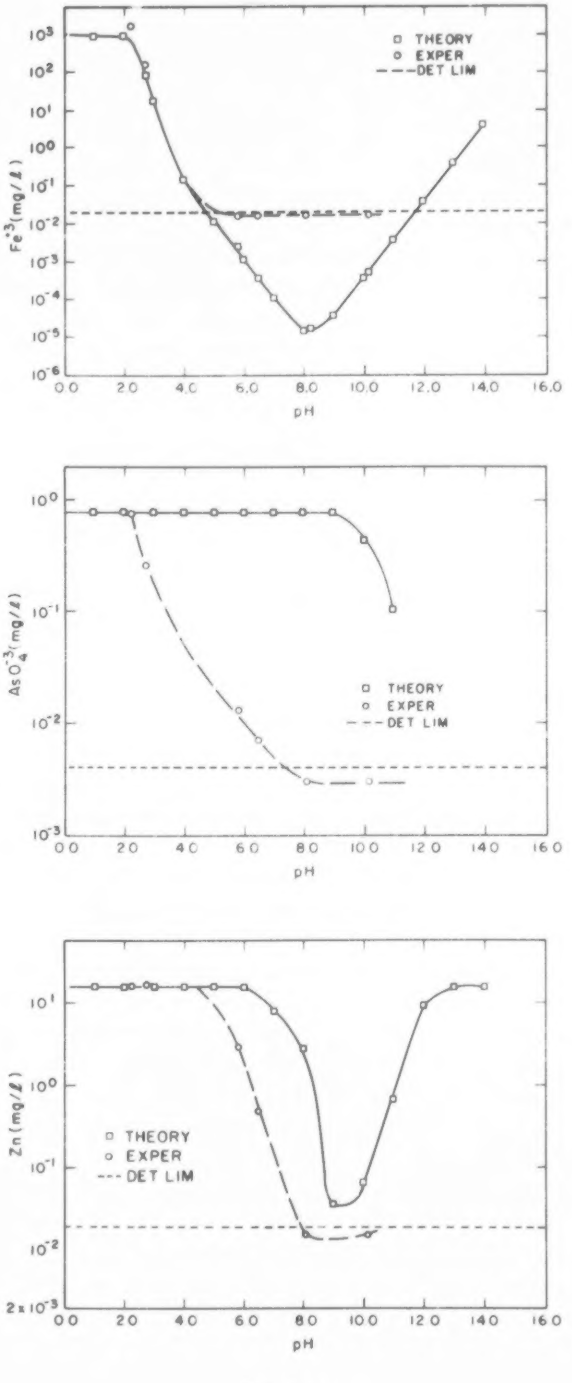

Fig. C-1.
Total soluble concentrations of iron, arsenic, and zinc vs pH as measured and as predicted by MINEQL.

significant solid forms of arsenate are predicted below a pH of 9 in this coal waste leachate. Laboratory measurements show arsenic concentrations lower than the detection limit of 0.01 mg/ℓ at pH 8.09 and 10.18. This is an approximate 500-fold discrepancy between measured and predicted concentrations indicating that some very important factor controlling AsO_4^{3-} chemistry in this system has been neglected. The value for Zn(II) is between the extremes shown by Fe(III) and AsO_4^{3-}. Predicted zinc concentrations decrease from 16 mg/ℓ at pH 4.0 to a minimum of ~0.02 mg/ℓ at pH 9.0 followed by a rapid increase to 10 mg/ℓ at pH 12. Predicted zinc chemistry is almost completely controlled by the formation of soluble free cation and $ZnSO_4$ ion pairs below pH 7. By pH 7 nearly half the zinc is precipitated as the silicate, which, together with the insoluble hydroxide, limits soluble zinc to low concentrations between pH 7 and 10. Above pH 11 the formation of the negatively charged $Zn(OH)_3^-$ complex begins to return zinc to a soluble form in appreciable quantities. In contrast to these predictions, measured zinc concentrations, after addition of $Ca(OH)_2$, begin to decrease at pH 5.82 and drop to significantly lower-than-predicted values (Fig. C-1) between pH 6 and 10. We have no measurements above pH 10.18 with which to compare predictions at higher pH.

Table C-II shows that the generally good agreement for F^- and Fe(II) is not found at pH 8.09 for Fe(II) or at pH 10.18 for F^-. At pH 8.09 measured Fe(II) concentration is 2.2 mg/ℓ, whereas that predicted is 14.7 mg/ℓ. For F^-, according to equilibrium calculations, 96% should be precipitated as CaF_2(s) at these pHs, but our measurements indicate that 13% of the fluoride remains in a soluble form. In contrast, at pH 6.49, the measured value corresponds somewhat better to that predicted. Predicted total F^- concentrations decrease slightly (from 4.0 to 2.6 mg/ℓ) between pH 5.82 and 10.18, inclusive (Table C-II), whereas measured values increase from 2.0 to 12.0 mg/ℓ in this interval. This suggests that pH is somehow affecting the measured result. A variety of factors could cause such an effect, including nonattainment of equilibrium at higher pH values.

Similar to arsenic and zinc, measured concentrations of cadmium, cobalt, chromium, copper, manganese, and nickel are comparable to predicted concentrations at pH 2.73. In general, measured values of these elements begin to diverge at values lower than predicted at pH 5.82 and

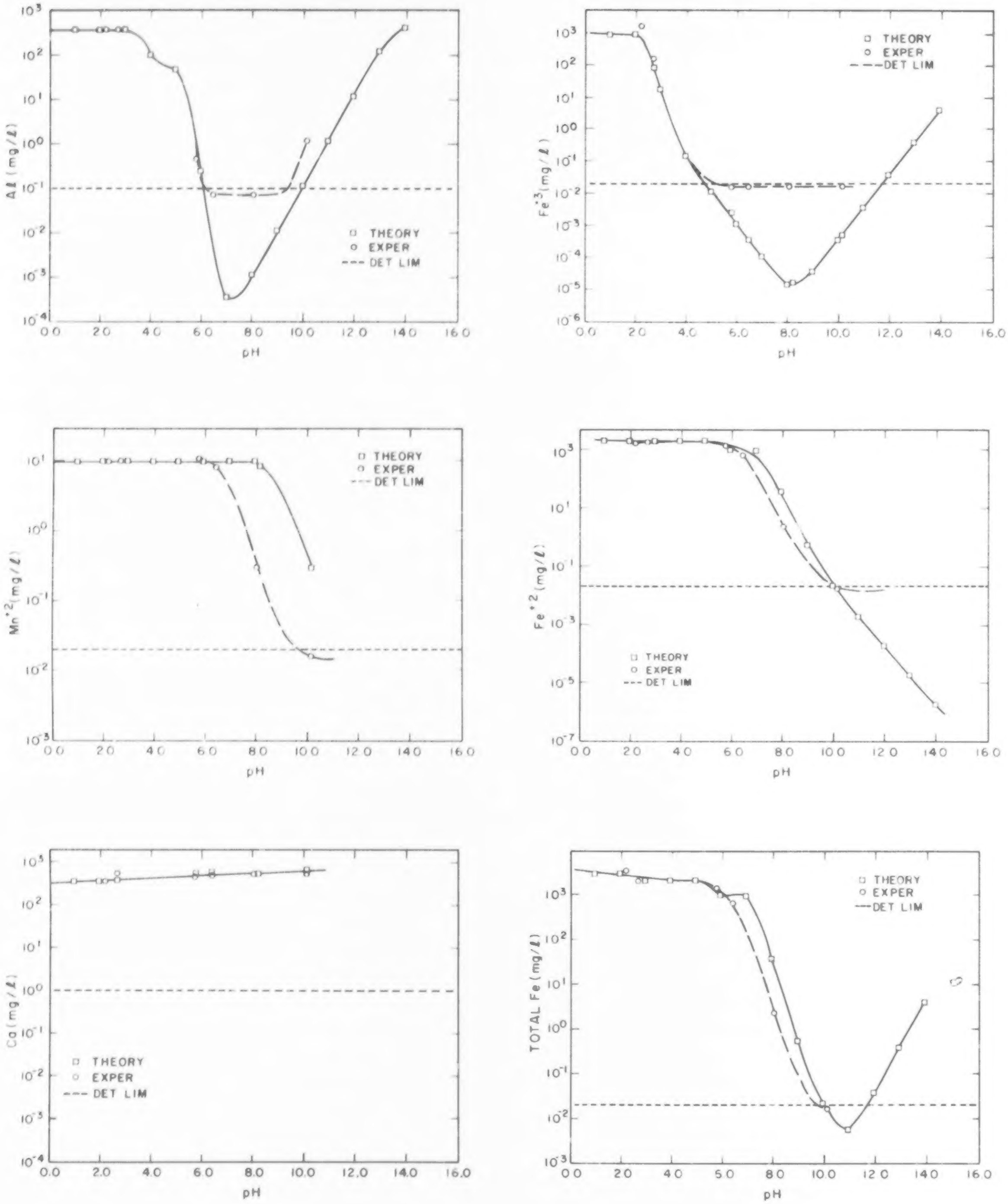

Fig. C-2a.
Total solution concentration vs pH for selected chemical components as predicted by a chemical equilibrium model and/or as measured following additions of $Ca(OH)_2$ to coal waste leachates.

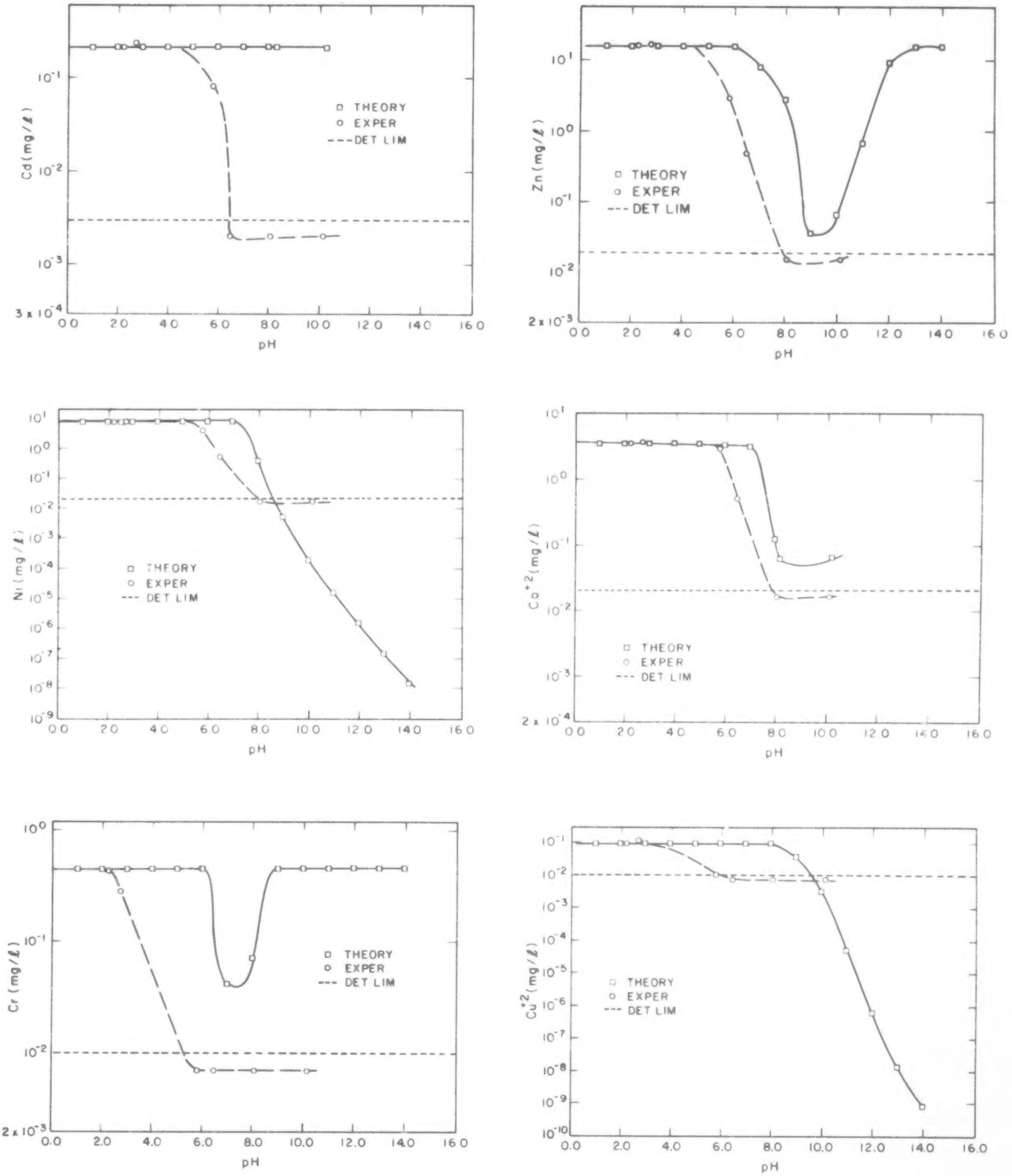

Fig. C-2b.

Total solution concentration vs pH for selected chemical components as predicted by a chemical equilibrium model and/or as measured following additions of $Ca(OH)_2$ to coal waste leachates.

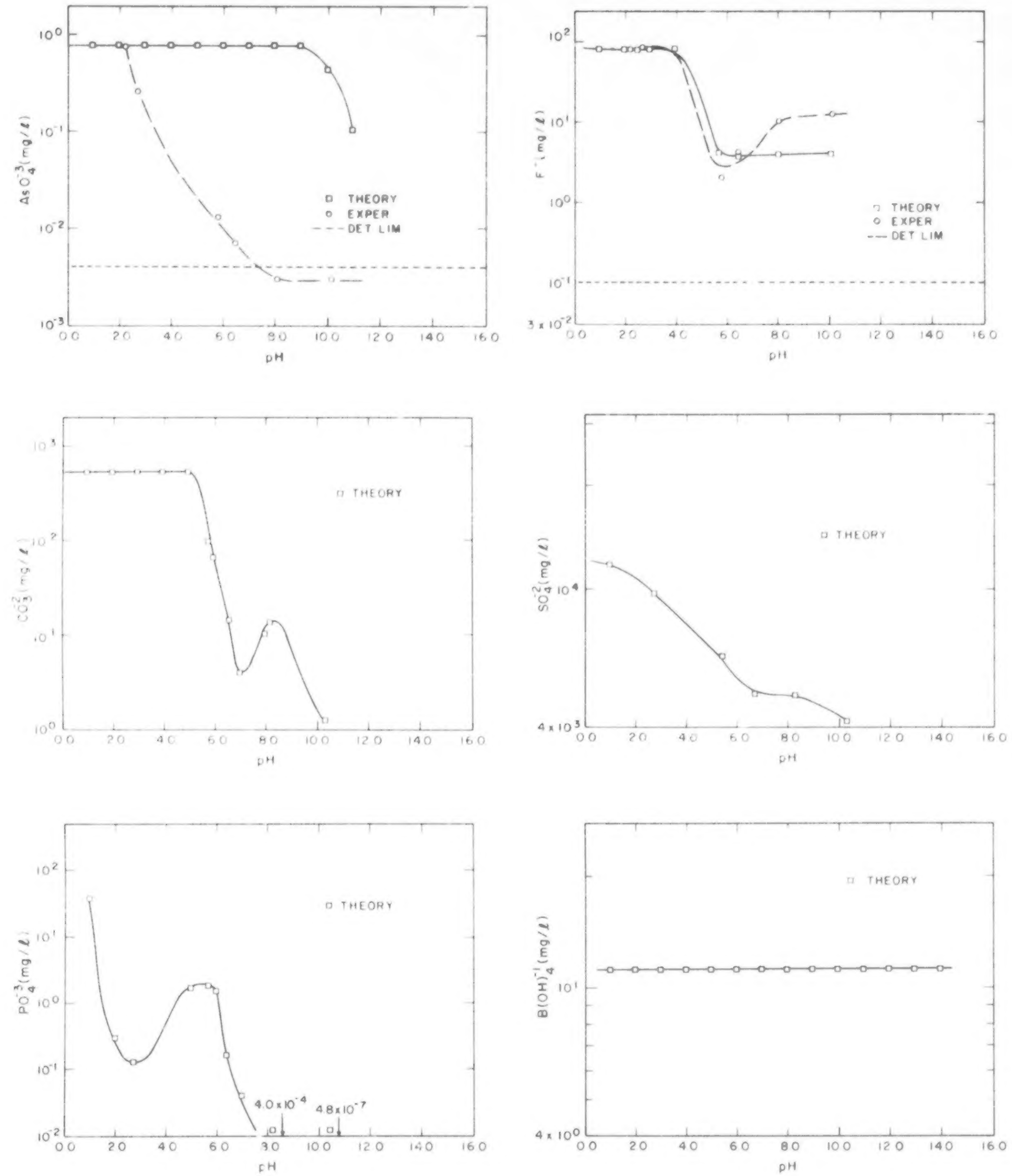

Fig. C-2c.

Total solution concentration vs pH for selected chemical components as predicted by a chemical equilibrium model and/or as measured following additions of $Ca(OH)_2$ to coal waste leachates.

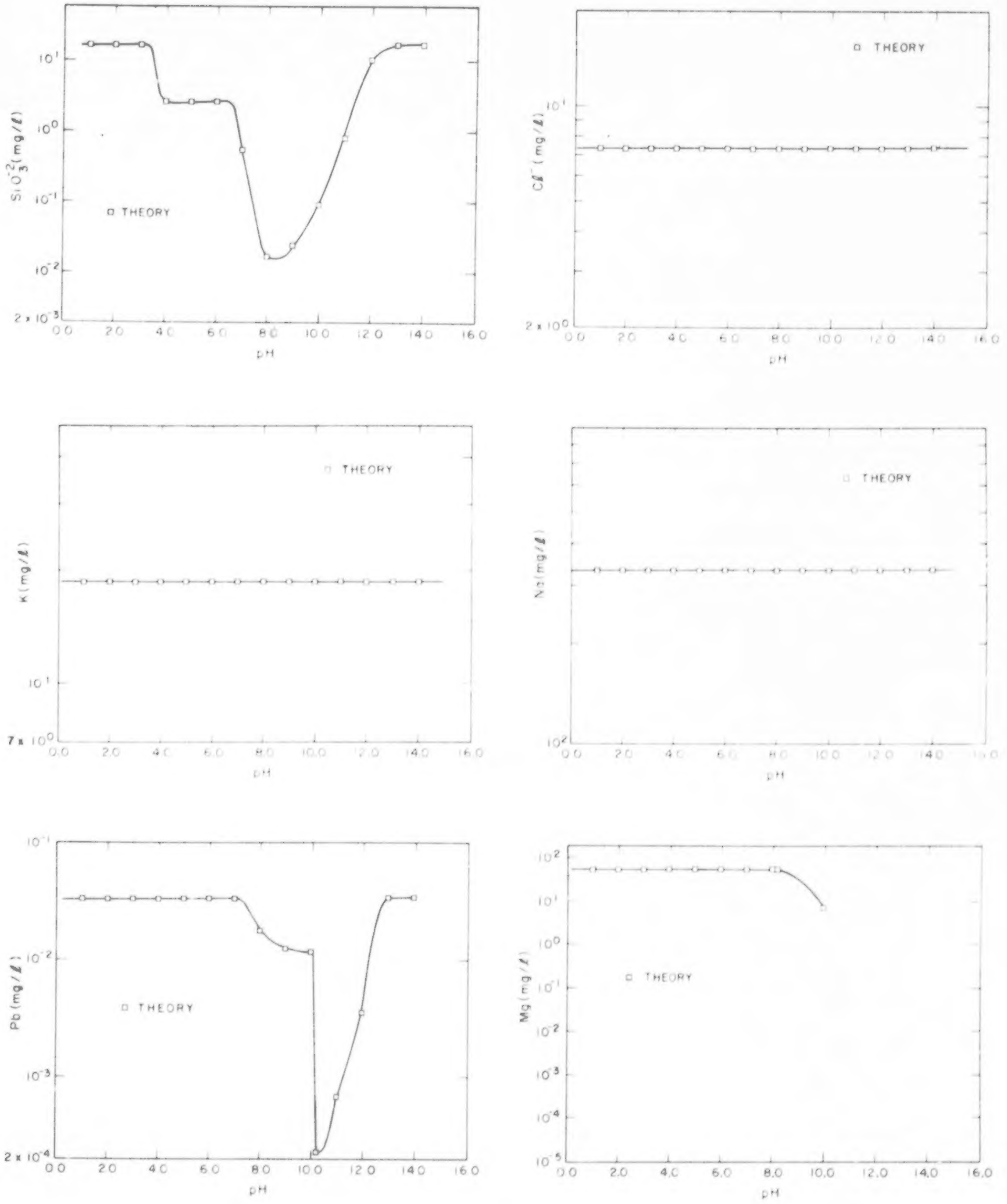

Fig. C-2d.
Total solution concentration vs pH for selected chemical components as predicted by a chemical equilibrium model and/or as measured following additions of $Ca(OH)_2$ to coal waste leachates.

above. Of these, measured concentrations of nickel are substantially lower than predicted at pH 6.49, but measured values of manganese are substantially lower than predicted only at pH 8.09. Thus, in all cases except F^-, measured concentrations fall below those predicted, often by a considerable amount.

B. Chemical Speciation of $Ca(OH)_2$-Treated Coal Refuse Leachate

Predicted equilibrium thermodynamic distributions of various initial components at acidic, near-neutral, and alkaline pH values, that is, pH of 2.73, 6.49, 8.09, and 10.18, are listed in Tables C-III through -VI. "Total Conc" values are those measured in the initial coal cleaning waste leachate, and for anion species, constitute the sum of unprotonated and protonated forms. "$\sum$ Soluble" values refer to the total concentrations of *all* soluble forms of that component. "Free Conc" values are the predicted solution concentrations of the unassociated free cation or anion. Predominant speciation of soluble forms is evident in the tables.

At pH 2.73 (Table C-III), three solids have precipitated, removing from solution a large fraction of the total Fe(III) and Ca and nearly all PO_4^{3-}. Solution concentrations of the generally quite soluble cation calcium are maintained at lower levels by the presence of high sulfate (0.123*M*) concentrations. Free ions and sulfate ion-pairs tend to dominate soluble forms of cations.

At pH 6.49 (Table C-IV), several more solid phases have appeared, effectively removing most aluminum from solution and reducing concentrations of CO_3^{2-}, Cr, F, Fe(II), PO_4^{3-}, SiO_3^{2-}, and Zn by varying amounts. At this pH all ferric iron is present as $Fe(OH)_3(s)$ and about 30% of the ferrous iron has precipitated as the carbonate. As at pH 2.73, cation soluble forms are dominated by free ions and sulfate complexes.

TABLE C–III

CALCULATED EQUILIBRIUM DISTRIBUTION OF CHEMICAL COMPONENTS IN COAL WASTE LEACHATE AFTER ADJUSTING TO pH 2.73 WITH $Ca(OH)_2$[a,b]

				SO_4^{2-}	CO_3^{2-}	PO_4^{3-}	F^-	Cl^-	SiO_3^{2-}	$B(OH)4^-$	AsO_4^{3-}	OH^-	Comment
	Total Conc			0.91	2.06	4.61	2.37	3.68	3.75	3.85	5.26		
		Free Conc		1.21	12.16	18.72	6.04	3.70	20.07	9.91	17.03		
Cations			Σ Soluble	1.02	2.06	5.82	2.37	3.68	3.75	3.85	5.26		
Ca(II)	1.43	2.23	2.01	2.40	6.78	11.29	7.80					12.02	73.9% as $CaSO_4$ (s)
Mg(II)	2.66	2.93	2.66	2.99	7.47	11.48	7.80					11.71	
K(I)	3.32	3.39	3.32	4.13									
Na(I)	1.84	1.87	1.84	3.01	13.45								
Fe(III)	1.53	4.25	2.90	3.01		7.83	5.24	7.49	5.11	6.20		3.74	95.6% as $Fe(OH)_3(s)$
Fe(II)	1.52	1.75	1.52	1.91				5.17				7.93	
Mn (II)	3.74	3.97	3.74	4.14	8.01	11.43		7.20				11.66	
Cu (II)	5.85	6.07	5.85	6.24	12.79	13.12	11.45	9.80		9.51		11.56	
Cd (II)	5.73	5.96	5.73	6.12	16.17	22.67	11.53	8.28				12.54	
Zn (II)	3.61	3.84	3.61	4.00		11.79	9.21	8.66				10.92	
Ni (II)	3.89	4.12	3.89	4.28			9.69	7.95				10.40	
Pb (II)	6.79	7.23	6.79	6.99	13.24			9.85		12.56		11.91	
Co (II)	4.23	4.55	4.23	4.51				8.37				11.33	
Cr (III)	5.09	6.90	5.09	5.09			8.69					8.10	
Al (III)	1.86	2.47	1.86	2.17			2.46					4.87	
H				2.37	5.32	9.90	6.10		10.32	3.85	8.90		
H_2					2.06	5.86			3.77		5.26		
H_3						6.90							
Comment					99.9% as H_2CO_3	93.8% as $FePO_4(s)$	99.7% complexed with Al		95.7% as H_2SiO_3	99.6 as $HB(OH)_4$	100% as H_2AsO_4		

Solid phases

$pFePO_4$ = 4.64
$pFe(OH)_3$ = 1.55
$pCaSO_4$ = 1.56

[a] All values given as negative logarithms of component in moles/liter, blank indicates species not present.

[b] Cation - anion complexes include all possible combinations of the components

TABLE C–IV

CALCULATED EQUILIBRIUM DISTRIBUTION OF CHEMICAL COMPONENTS IN COAL WASTE LEACHATE AFTER ADJUSTING TO pH 6.49 WITH CA(OH)$_2$[a,b]

Cations	Total Conc	Free Conc	% Soluble	SO_4^{2-}	CO_3^{2-}	PO_4^{3-}	F^-	Cl^-	SiO_3^{2-}	$B(OH)_4^-$	AsO_4^{3-}	OH^-	Comment
Total Conc				0.91	2.06	4.61	2.37	3.68	3.75	3.85	5.26		
Free Conc				1.39	7.12	11.55	3.80	3.69	13.3	6.15	9.88		
% Soluble				1.28	3.89	6.00	3.78	3.68	4.55	3.85	5.26		
Ca(II)	1.06	2.04	1.89	2.40	5.30	7.68	5.39					8.08	82.5% as $CaSO_4(s)$
Mg(II)	2.66	2.85	2.66	3.10	6.11	7.99	5.48					7.88	
K(I)	3.32	3.37	3.32	4.29									
Na(I)	1.84	1.86	1.86	3.17	8.40								
Fe(III)	1.53	15.53	8.19	14.73		15.70	13.9	18.76	13.42	13.35		8.19	All as $Fe(OH)_3(s)$
Fe(II)	1.52	1.63	1.79	2.19				5.25				4.25	29% as $FeCO_3(s)$
Mn(II)	3.74	3.90	3.74	4.25	6.67	7.95		7.13				7.83	
Cu (II)	5.85	6.42	5.85	6.76	8.09	10.06	9.55	10.14		6.07		8.14	
Cd(II)	5.73	5.89	5.73	6.24	11.06	15.4	9.22	8.22				8.72	
Zn(II)	3.61	3.92	3.75	4.26		8.46	7.04	8.74				7.24	29% as $ZnSiO_3$ (s)
Ni(II)	3.89	4.05	3.89	4.40			7.38	7.88				6.58	
Pb(II)	6.79	7.17	6.79	7.12	8.14			9.80		8.65		8.10	
Co(II)	4.23	4.46	4.32	4.61				8.28				7.48	
Cr(III)	5.09	8.93	5.59	7.30			8.37					5.60	69% as $Cr(OH)_3$ (s)
Al(III)	1.86	11.13	7.07	11.06			7.07					8.84	99.4% as $Al(OH)_3$ (s)
H				6.30	4.03	6.48	7.60		7.35	3.85	5.51		
H_2					4.54	6.21			4.55		5.63		
H_3						11.01							
Comment				58% as $CaSO_4(s)$	95.9% as $FeCO_3(s)$	95.9% as $Fe_3(PO_4)_2(s)$	96.2% as $CaF_2(s)$		84% as $ZnSiO_3(s)$ or $Al_2(SiO_3)_2$ OH (s)	99% as $HB(OH)_4$			

Solid Phases

p CaF_2 = 2.69; $pCaSO_4$ = 1.15

p $FeCO_3$ = 2.07; $pFe_3(PO_4)_2$ = 4.93

p $Fe(OH)_3$ = 1.53

p $Al(OH)_3$ = 1.87; $pAl_2(SiO_3)_2(OH)_2$ = 4.40

$pZnSiO_3$ = 4.15

p $Cr(OH)_3$ = 5.25

a All values given as negative logarithms of component in moles/liter, blank indicates species not present

b Cation - Anion complexes include all possible combinations of the components

At pH 8.09 (Table C-V), all phosphate is now present as $Ca_5(PO_4)_3OH(s)$. Ferrous iron concentrations have been lowered even further because of the formation of $Fe(OH)_2(s)$ at this concentration of OH^-. $MnCO_3(s)$ and $MnSO_4(s)$ have appeared for the first time, removing a fraction of manganous ion from solution. Several other insoluble phases appear or become increasingly important, for example, $CoCO_3(s)$, and the hydroxides of Zn, Ni, Pb, and Cr. No solid phases are indicated for $B(OH)_4^-$ or AsO_4^{3-} at this pH. In addition to soluble sulfate complexes, hydroxy complexes become important at this pH.

At pH 10.18 (Table C-IV), insoluble hydroxides are the dominant solid phase for all cations except calcium and zinc. No solid phases containing boron, cadmium, or chromium are predicted at this pH. Predicted total solution concentrations are quite low for all components except calcium, arsenic, boron, cadmium, and chromium compared with initial values. The precipitation of $Ca_3(AsO_4)_2$ at this pH accounts for 37% of the total AsO_4^{3-}. At this pH, Cr(III) is soluble as the $Cr(OH)_4^-$ complex, whereas at pH 8.09, it was present as insoluble $Cr(OH)_3(s)$. Negatively charged hydroxy complexes are important in speciation of soluble components at this pH. Sulfate complexes are no longer very important.

IV. DISCUSSION

These laboratory and theoretical results have shown some reasons that lime addition is a most effective method for controlling contaminant levels in acidic waters from coal mine and coal cleaning residue drainages. Added hydroxide ions are consumed by the

TABLE C–V

CALCULATED EQUILIBRIUM DISTRIBUTION OF CHEMICAL COMPONENTS IN COAL WASTE LEACHATE AFTER ADJUSTING TO pH 8.09 WITH $Ca(OH)_2$[a,b]

Cations	Total Conc	Free Conc	%Soluble	SO_4^{2-}	CO^{2-}	PO_4^{3-}	F^-	Cl^-	SiO_3^{2-}	$B(OH)_4^-$	AsO_4^{3-}	OH^-	
				0.91	2.06	4.61	2.37	3.68	2.75	3.85	5.26		
				1.46	5.18	12.01	3.83	3.68	12.38	4.63	8.04		
				1.39	3.65	8.47	3.81	3.68	6.78	3.85	5.26		
Ca (II)	1.00	1.99	1.84	2.40	4.90	9.69	5.35					6.41	83% as $CaSO_4(s)$
Mg (II)	2.66	2.83	2.66	3.14	5.58	10.03	5.48					6.26	
K (I)	3.32	3.36	3.32	4.35									
Na (I)	1.84	1.86	1.84	3.24	6.47								
Fe(III)	1.53	20.33	9.62	19.39		22.55	18.96	23.55	18.87	15.35		9.62	100% as $FeOH)_3(s)$
Fe(II)	1.52	3.77	3.58	4.18				7.18				4.59	99% as $Fe(OH)_2(s)$ + $FeCO_3(s)$
Mn(II)	3.74	3.82	3.82	4.38	6.39	10.06		7.18				6.29	39% as $MnCO_3(s)$ + $MnSo_4(s)$
Cu(II)	5.85	8.21	5.85	8.62	7.94	13.91	11.37	[illegible]		5.86		8.33	98% as $Cu(B(OH)_4)_2$ and $CuB(OH)_4^+$
Cd(II)	5.73	5.89	5.73	6.31	9.13	15.89	9.26	8.21				7.11	
Zn(II)	3.61	4.87	4.72	5.28		11.46	8.03	9.68				6.57	92% as $ZnSiO_3(s)$ + $Zn(OH)_2(s)$
Ni(II)	3.89	5.77	5.59	6.18			9.13	9.58				6.69	98% as $Ni(OH)_2(s)$
Pb(II)	6.79	8.57	7.16	8.58	7.60			11.18		7.62		7.87	58% as $Pb(OH)_2(s)$
Co(II)	4.23	6.37	6.15	6.58				10.18				7.75	98.7% as $CoCO_3(s)$
Cr(III)	5.09	13.73	5.78	12.17			13.20					5.80	80.7% as $Cr(OH)_3(s)$
Al(III)	1.86	15.93	7.30	15.94			11.96					7.30	100 % as $Al(OH)_3(s)$
H				7.97	3.70	8.54	9.24		8.00	3.93	5.27		
H_2					5.80	9.86			6.80		6.99		
H_3						16.3							
Comment				67.1 % as $CaSO_4(s)$	96.4% as $FeCO_3(s)$	100% as $Ca_5(OH)\cdot(PO_4)_3(s)$	96% as $CaF_2(s)$	99.9% as free ion	99.9% as $ZnSiO_3(s)$	98.3% as free or protonated form	99.9% in protonated		

Solid Phases

$pCa_5(PO_4)_3OH$ = 5.09, $pCaF_2$ = 2.69, $pCaSO_4$ = 1.08

$pFe(OH)_2$ = 1.67 $pFeCO_3$ = 2.08

$pFe(OH)_3$ = 1.53

$pPb(OH)_2$ = 7.03

$pNi(OH)_2$ = 3.90

$pZnSiO_3$ = 3.75, $pZn(OH)_2$ = 4.32

$pAl(OH)_3$ = 1.86

$pCoCO_3$ = 4.23

$pCr(OH)_3$ = 5.18

$pMnCO_3$ = 4.54

a All values given as negative logarithm of component in moles/liter, blank indicates species not present

b Cation-anion complexes include all possible combinations of components

neutralization of hydronium ion and by the precipitation of ferric and other metallic hydroxides. Although not investigated here, oxidation of iron from the more soluble ferrous to ferric state also proceeds much more rapidly at elevated pH as does the oxidation of manganous to manganic ion. For these reasons alkaline neutralization followed by oxidative aeration is a widely favored method of pollution control by the coal processing industry.[2]

The principal purposes of this study were to investigate the effectiveness of this method in removing a number of trace components from solution and to relate these results to model predictions that might allow the behavior of numerous other unmeasured species to be predicted. Good general agreement between measured and predicted values was indeed found for several components. However, a surprising result of this work was that predictions of solution concentrations for some components were higher than were measured in the laboratory. Thus, the measured concentrations of trace and minor components are generally lower than those predicted from precipitation and dissolution of solid phases alone. This also appears to be the case for ferrous iron (a dominant constituent) at neutral pH. As an example, Table C-II shows measured cadmium concentrations to be substantially lower than those predicted at

TABLE C–VI

CALCULATED EQUILIBRIUM DISTRIBUTION OF CHEMICAL COMPONENTS IN COAL WASTE LEACHATE AFTER ADJUSTING TO pH 10.18 WITH Ca(OH)$_2$[a,b]

Cations	Total Conc	Free Conc	% Soluble	SO_4^{2-}	CO_3^{2-}	PO_4^{3-}	F^-	Cl^-	SiO_3^{2-}	$B(OH)^-_4$	AsO_4^{3-}	OH^-	Comment
Total Conc				0.910	2.06	4.61	2.37	3.68	3.75	3.85	5.26		
Free Conc				1154	5.14	12.85	3.88	3.68	8.20	3.86	6.24		
% Soluble				1.48	4.83	11.41	3.86	3.68	5.85	3.85	5.49		
Ca(II)	0.93	1.90	1.78	2.40	5.29	12.53	5.31					4.24	85.8% bound in solid phases
Mg(II)	2.66	3.65	3.48	4.04	6.84	13.77	6.35					4.98	85.1% as $Mg(OH)_2(s)$
K(I)	3.32	3.36	3.32	4.43									
Na(I)	1.84	1.86	1.84	3.32	6.42								
Fe(III)	1.53	26.60	8.01	25.76		31.75	25.76	29.82	23.05	20.10		8.01	100% as $Fe(OH_3(s)$
Fe(II)	1.52	7.95	6.65	8.44				11.36				6.68	100% as $Fe(OH)_2(s)$
Mn(II)	3.74	5.55	5.27	6.04	10.02	14.57		8.76				5.78	97.0% as $Mn(OH)_2(s)$
Cu(II)	5.85	12.05	8.28	12.54	11.73	20.67	15.25	15.76		8.29		8.32	99.[illegible]% as $Cu(OH)_2(s)$
Cd(II)	5.73	7.01	5.73	7.50	10.20	17.84	10.41	9.32				5.76	
Zn(II)	3.61	9.05	5.80	9.54		18.57	12.25	13.86				5.80	72.1% as $ZnSiO_3(s)$;27.3% as $Zn(OH)_2$(s
Ni(II)	3.89	9.95	8.74	10.44			13.35	13.76				8.78	100% as $Ni(OH)_2(s)$
Pb(II)	6.79	12.75	8.99	12.84	11.73			15.36		10.31		9.08	99.4% as $Pb(OH)_2(s)$
Co(II)	4.23	7.95	6.15	8.24				11.76				6.20	98.8% as $Co(OH)_2$ (s)
Cr(III)	5.09	21.36	5.09	19.90			20.90					5.09	100% as $Cr(OH)_4^-$
Al(III)	1.86	22.20	5.21	22.32			18.33					5.21	100% as $Al(OH)_3$ (s)
H				10.15	5.75	11.47	11.37		5.91	5.26	5.56		
H_2					9.94	14.88			6.80		9.37		
H_3						23.37							
Comment				72.9% as $CaSO_4(s)$	99.8% as $CaCO_3(s)$	100% as $Ca_5(PO_4)_3OH(s)$	96.8% as $CaF_2(s)$		99.2% as $ZnSiO_3(s)$	96.1% as $B(OH)_4^-$	37% as $Ca_3(AsO_4)_2$		

Solid phases

$pFe(OH)_2$ = 1.52
$pFe(OH)_3$ = 1.53
$pAl(OH)_3$ = 1.86
$pCaCO_3$ = 2.06, $pCaF_2$ = 2.69, $pCaSO_4$ = 1.05; $pCa_5(PO_4)_3OH$ = 5.09; $pCa_3(AsO_4)_2$ = 5.99
$pMn(OH)_2$ = 3.76
$pMg(OH)_2$ = 2.73
$pPb(OH)_2$ = 6.80
$pCu(OH)_2$ = 5.85
$pNi(OH)_2$ = 3.89
$pCo(OH)_2$ = 4.23
$pZn(OH)_2$ = 4.18; $pZnSiO_3$ = 3.75

[a] All values given as negative logarithms of component in moles/liter, blank indicates species not present

[b] Cation - anion complexes include all possible combinations of the components

all pH values from 5.82 through 10.18. The predicted cadmium values are nearly 100-fold too high at pH 6.49 and 8.09.

In view of what is known about coal cleaning waste leachates, the facts that the two major cations (aluminum and iron), are well accounted for in these calculations, and that a charge balance within 10% is obtained, make it unlikely that any significant ligands have been omitted from the thermodynamic calculations. Consequently, we do not believe that some unknown solid phases can be invoked to account for the lower measured concentrations. The major cation components in these solutions form amorphous hydrous solid phases at all measured pH. In fact, at pH greater than ~2.5, most of the Fe(III) present in the initial leachate occurs as $Fe(OH)_3(s)$. The analogous situation is true for aluminum at pH greater than ~5.5. Thus at pH > 5.5, 2.92×10^{-2} moles of $Fe(OH)_3(s)$ and 1.37×10^{-2} moles of $Al(OH)_3(s)$ are available per liter of leachate in a finely dispersed form for adsorption of other components in solution. Removal of trace species from solution by adsorption onto these hydrous oxides seems highly probable. In addition to ferric and aluminum hydroxides, substantial quantities of other solid phases, $CaSO_4(s)$, $Fe(OH)_2(s)$, $FeCO_3(s)$, and $CaF_2(s)$, are present. The adsorption properties of these solids may also aid in removing minor and trace species from this experimental solution.

Different investigators[7-9] have shown that substantial quantities of various trace components are removed from solution by adsorption onto the surfaces of hydrous oxides. For example, Ref. 7 shows that at pH 7.0, 6.25 mmole/ℓ of hydrous ferric oxide removes more than 10% of the Zn(II) and Cd(II) from solutions containing 1.0 mmole/ℓ of these species. These adsorption values increased rapidly to 60-70% adsorption at pH 8. Our solution contained 0.24 mmoles of Zn(II), 1.86×10^{-3} mmoles Cd(II) and 29.2 mmoles of $Fe(OH)_3(s)$ per liter of solution. Thus, sufficient adsorption capacity is apparently available to have a significant effect on solution concentrations of trace or minor species, such as cadmium and zinc.

Sufficient available adsorbing surface does not necessarily mean that all or even a large fraction of a certain species will be adsorbed. The quantity adsorbed is dependent on, among other things, the equilibrium concentration of the adsorbed species. Thus, adsorption can be treated in a manner analogous to the thermodynamic approach used in MINEQL by including an equilibrium expression between sorption and desorption. Such models incorporating sorption/desorption have recently been added to computer equilibrium codes based on the original MINEQL program.[10,11] Analysis by such a program of the coal cleaning waste leachate system presented here is planned as a part of future work in this area.

In summary, these results show that application of chemical thermodynamic principles to a problem in environmental control can assist in understanding mechanisms and factors controlling the solubility of components. Although the equilibrium assumption was not explicitly tested, kinetic arguments are not needed to explain discrepancies between laboratory and calculated concentrations.

REFERENCES

1. E. M. Wewerka, J. M. Williams, N. E. Vanderborgh, A. W. Harmon, P. Wagner, P. L. Wanek, and J. D. Olsen, "Trace Element Characterization of Coal Wastes—Second Annual Progress Report," Los Alamos Scientific Laboratory report LA-7360-PR, US Environmental Protection Agency report EPA-600/7-78-08 (July 1978).

2. Roger C. Wilmouth, "Limestone and Lime Neutralization of Ferrous Iron Acid Mine Drainage," US Environmental Protection Agency report EPA-600/2-77-101 (May 1977).

3. D. K. Nordstrom, L. N. Plummer, T. M. L. Wigley, T. J. Wolery, J. W. Ball, E. A. Jenne, R. L. Bassett, D. A. Crerar, T. M. Florence, B. Fritz, M. Hoffman, G. R. Holdren, Jr., G. M. Lafon, S. V. Mattigod, R. E. McDuff, F. Morel, M. M. Reddy, G. Sposito, J. Thrailkill, "Comparison of Computerized Chemical Models for Equilibrium Calculations in Aqueous Systems," in *Chemical Modeling in Aqueous Systems*, E. A. Jenne, Ed. (American Chemical Society, 1979), Chap. 38, pp. 857-892.

4. Francois Morel and James Morgan, "A Numerical Method for Computing Equilibria in Aqueous Chemical Systems," Environ. Sci. Technol. 6, 58-67 (1972).

5. C. W. Davies, *Electrochemistry* (Philosophical Library, London, 1967).

6. Darrell K. Nordstrom, Everett A. Jenne, and James W. Ball, "Redox Equilibria of Iron in Acid Mine Waters," in *Chemical Modeling in Aqueous Systems*, E. A. Jenne, Ed. (American Chemical Society, 1979), Chap. 3, pp. 51-79.

7. R. Rao Gadde and Herbert A. Laitinen "Studies of Heavy Metal Adsorption by Hydrous Iron and Manganese Oxides," Anal. Chem. 46, 2022-2026 (1974).

8. Everett A. Jenne, "Controls on Mn, Fe, Co, Ni, Cu, and Zn Concentrations in Soils and Water: the Significant Role of Hydrous Mn and Fe Oxides," in *Trace Inorganics in Water*, R. F. Gould, Ed. (American Chemical Society, 1968), Chap. 21, pp. 337-387.

9. Robert O. James and Thomas W. Healy, "Adsorption of Hydrolyzable Metal Ions at the Oxide-water Interface I. Co(II) Adsorption on SiO_2 and TiO_2 as Model Systems," J. Colloid Interface Sci. **40**, 42-52 (1972).

10. Sara E. Ingle, James A. Kemiston, and Donald W. Schultz, "REDEQL. EPAK: Aqueous Chemical Equilibrium Computer Program," Corvallis Environmental Research Laboratory, Corvallis, Oregon, US Environmental Protection Agency report EPA-600/3-80-049 (May 1980).

11. Shas V. Mattigod and Garrison Sposito, "Chemical Modeling of Trace Metal Equilibria in Contaminated Soil Solutions Using the Computer Program GEOCHEM," in *Chemical Modeling in Aqueous Systems*, E. A. Jenne, Ed. (American Chemical Society, 1979), Chap. 37, pp. 837-856.

APPENDIX D

GENERAL INFORMATION ON COAL PREPARATION PLANTS I AND K

TABLE D-I

INFORMATION ON PREPARATION PLANT I

Date sampled:	5/1/79 for 4 h	
Location:	Western Pennsylvania	
Coal seams:	Purchased coal that is blended	
	Old piles and seconds	37%
	Deep mines-Lower Kittanning	29%
	Strip mines-Upper Kittanning	7%
	-Lower Freeport	27%
Feed coal properties:	Company data, March 1979	
	Moisture (%)	4.53
	Ash (%, dry)	13.96
	Sulfur (%, dry)	2.89
	Btu	12 500
	% Float	65
Cleaning equipment:	−3/4-in. rotary breaker	
	Cyclones	
	−3/4-in. clean coal	
Feed rate:	500 ton/h	
Sampled:	Raw coal before breaker	4 × 13 gal.
	Cleaned and dried	4 × 13 gal.
	Refuse and breaker reject	4 × 13 gal.
Waste disposal:	Conveyored; thin-layered in shallow valley; clay-lined with drainage ditches; effluent collected and treated with mine water at lime plant. 500 × 1500 ft pile, 20 ft. high. Uncovered without evidence of intermittent cover.	

TABLE D-II

INFORMATION ON PREPARATION PLANT K

Date sampled:	5/3/79 for 3 h	
Location:	Western Pennsylvania	
Coal seams:	Purchased coal that is blended Upper and Lower Kittanning Upper and Lower Freeport	
Cleaning equipment:	–5-in. crusher 1 cell, Jeffery jig –2-in. clean coal –3/8-in. bypass	
Feed rate:	150 ton/h	
Sampled:	Raw coal (5 × 3/8)	4 × 13 gal.
	Raw coal/"clean" coal (3/8 × 0)	2 × 13 gal.
	Clean coal (2 × 3/8)	4 × 13 gal.
	Refuse (5 × 10) 60/40 fine/coarse split	4 × 13 gal.
Observations:	pH adjusted in washing water with soda ash	
Waste disposal:	Trucked back to strip mine	

APPENDIX E

RESULTS OF STATIC AND DYNAMIC LEACHING EXPERIMENTS WITH COAL AND COAL WASTE SAMPLES FROM PLANT K

TABLE E–I

AVERAGE LEACHATE COMPOSITIONS FROM STATIC LEACHING EXPERIMENTS WITH COAL PREPARATION WASTES FROM PLANT K

Time (Days)	pH	Cond (μmho/cm)	Be (ppm)	Al (ppm)	Mn (ppm)	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Se (ppm)	Cd (ppm)	Pb (ppm)
1	3.0	1140	0.012	4.7	3.3	181	0.63	1.0	0.66	1.0	0.05	0.002	0.010	0.15
5	2.9	1520	0.023	9.9	3.1	295	0.84	1.3	0.82	2.0	0.06	<0.002	0.017	<0.01
25	2.0	5200	0.046	72	24	1940	1.22	1.8	3.74	5.7	3.0	0.04	0.041	<0.01
50	1.6	14400	0.043	110	23	9250	1.56	2.8	2.60	6.5	18.0	0.57	0.059	<0.01

TABLE E–II

AVERAGE LEACHATE COMPOSITIONS FROM STATIC LEACHING EXPERIMENTS WITH FEED COAL FROM PLANT K

Time (Days)	pH	Cond (mmho/cm)	Be (ppm)	Al (ppm)	Mn (ppm)	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Se (ppm)	Cd (ppm)	Pb (ppm)
1	2.8	0.97	0.007	5.5	0.8	86	0.35	0.5	0.30	1.1	0.01	<0.001	0.008	0.06
5	2.5	1.13	<0.005	7.4	1.1	135	0.37	0.6	0.43	1.5	0.03	<0.001	0.009	0.03
25	2.4	3.35	0.007	18	6.2	930	0.61	0.8	0.15	2.5	0.3	0.02	0.016	0.02
50	2.2	3.20	0.012	16	2.6	580	0.68	1.0	1.07	3.1	0.4	0.01	0.028	0.05

TABLE E–III

AVERAGE LEACHATE COMPOSITIONS FROM STATIC LEACHING EXPERIMENTS WITH CLEANED COAL FROM PLANT K

Time (Days)	pH	Cond (mmho/cm)	Be (ppm)	Al (ppm)	Mn (ppm)	Fe (ppm)	Co (ppm)	Ni (ppm)	Cu (ppm)	Zn (ppm)	As (ppm)	Se (ppm)	Cd (ppm)	Pb (ppm)
1	2.5	2.60	0.012	35	3.9	650	0.80	1.0	0.74	3.3	0.6	0.02	0.025	0.04
5	2.4	2.40	0.013	35	4.4	770	0.73	1.0	0.74	3.4	0.3	0.008	0.024	0.02
25	2.3	3.95	0.023	45	4.5	1040	0.88	1.2	0.88	3.8	1.3	0.02	0.026	<0.01
50	2.2	3.80	0.024	49	4.7	890	0.92	1.3	1.15	6.1	1.4	0.04	0.032	0.01

TABLE E–IV

RESULTS OF DYNAMIC LEACHING EXPERIMENT GL–30 ON COAL WASTE FROM PLANT K

Sample	Time (hrs)	Cum Vol (mℓ)	g H_2O/ g waste	pH	Cond (mmho/cm)
30– 1	17.5	86	0.174	2.00	8.30
30– 2	20.3	176	0.356	2.05	7.40
30– 3	23.0	251	0.508	2.06	6.50
30– 4	39.5	524	1.06	2.35	4.65
30– 5	42.5	602	1.22	2.66	2.63
30– 6	45.0	682	1.38	2.75	2.28
30– 7	46.0	761	1.54	2.85	1.99
30– 8	63.5	1021	2.07	2.92	1.60
30– 9	65.5	1101	2.23	3.08	1.32
30– 10	67.5	1185	2.40	3.14	1.14
30– 11	70.5	1265	2.56	3.19	1.03
30– 12	88.1	1780	3.60	3.36	0.61
30– 13	91.1	1862	3.77	3.34	0.45
30– 14	–	1942	3.93	3.40	0.37
30– 15	116.8	2622	5.31	3.56	0.25
30– 16	160.2	3882	7.86	3.61	1.42
30– 17	163.8	3961	8.02	3.82	0.98
30– 18	166.0	4043	8.18	3.85	1.00
30– 19	543.5	4554	9.22	2.27	5.40
30– 20	546.0	4647	9.41	2.34	4.50
30– 21	550.0	4741	9.58	2.44	3.55
30– 22	552.0	4861	9.84	2.51	3.10
30– 23	567.5	5436	11.0	2.79	1.59
30– 24	570.0	5534	11.2	3.02	0.86
30– 25	573.0	5631	11.4	3.09	0.76
30– 26	575.5	5731	11.6	3.12	0.67
30– 27	591.5	6306	12.8	3.18	0.46
30– 28	595.0	6434	13.0	3.46	0.28
30– 29	597.2	6517	13.2	3.51	0.24
30– 30	599.8	6604	13.4	3.50	0.27

TABLE E–V

RESULTS OF DYNAMIC LEACHING EXPERIMENT GL–31 ON COAL WASTE FROM PLANT K

Sample	Time (hrs)	Cum Vol (mℓ)	g H_2O/ g waste	pH	Cond (mmho/cm)
31– 1	17.0	86	0.172	2.00	8.80
31– 2	20.5	174	0.347	2.05	7.80
31– 3	23.5	257	0.513	2.12	6.90
31– 4	39.5	465	0.928	2.21	5.80
31– 5	43.5	552	1.10	2.50	3.68
31– 6	46.5	633	1.26	2.58	3.12
31– 7	64.1	1183	2.36	2.90	1.70
31– 8	67.5	1270	2.54	3.11	0.84
31– 9	–	1351	2.70	3.14	0.71
31– 10	93.0	1941	3.87	3.33	0.45
31– 11	136.4	2681	5.35	3.62	0.24
31– 12	140.0	2757	5.50	3.71	0.24
31– 13	143.5	2845	5.68	3.78	0.20
31– 14	160.2	3180	6.35	3.81	0.17
31– 15	162.8	3267	6.52	3.98	0.12
31– 16	164.5	3353	6.69	3.99	0.11
31– 17	166.5	3437	6.86	4.03	0.11
31– 18	168.0	3536	7.06	4.06	0.07
31– 19	183.5	4316	8.62	4.01	0.08

TABLE E–VI

RESULTS OF DYNAMIC LEACHING EXPERIMENT GL–32 ON COAL WASTE FROM PLANT K

Sample	Time (hrs)	Cum Vol (mℓ)	g H_2O/ g waste	pH	Cond (mmho/cm)
32– 1	16.0	78	0.137	1.93	8.90
32– 2	18.5	167	0.294	1.99	7.80
32– 3	21.0	246	0.433	2.04	7.20
32– 4	23.5	320	0.563	2.10	6.25
32– 5	39.5	590	1.04	2.34	4.20
32– 6	43.0	695	1.22	2.66	2.22
32– 7	48.0	817	1.44	2.78	1.80
32– 8	63.5	1087	1.91	2.95	1.33
32– 9	65.5	1168	2.06	3.09	1.03
32– 10	68.5	1280	2.25	3.15	0.86
32– 11	72.0	1380	2.43	3.31	0.71
32– 12	88.1	1915	3.37	3.39	0.47
32– 13	91.0	2028	3.57	3.36	0.33
32– 14	–	2139	3.77	3.46	0.29
32– 15	117.0	2839	5.00	3.62	0.21
32– 16	160.6	4239	7.46	3.85	0.14
32– 17	163.5	4329	7.62	3.92	0.11

TABLE E–VII

RESULTS OF DYNAMIC LEACHING EXPERIMENT GL–33 ON COAL WASTE FROM PLANT K

Sample	Time (hrs)	Cum Vol (mℓ)	g H_2O/ g waste	pH	Cond mmho/cm	Fe (ppm)	Ni (ppm)	Mn (ppm)	Zn (ppm)	Cd (ppm)	Al (ppm)	Cu (ppm)	As (ppm)	Co (ppm)	Pb (ppm)	Be (ppm)	Se (ppm)	Ag (ppm)	Ba (ppm)
33– 1	17.2	105	0.205	2.14	6.80	2410	4.8	20.0	10.5	0.10	95	3.38	2.2	3.14	0.60	0.09	0.02	<0.01	<0.1
33– 2	20.5	203	0.396	2.20	6.00	1920	4.1	17.2	10.0	0.07	79	2.64	1.6	2.81	0.43	0.08	0.01	<0.01	<0.1
33– 3	23.8	301	0.588	2.27	5.20	1600	3.3	14.9	7.8	0.06	65	1.99	1.1	2.31	0.30	0.07	0.02	0.06	<0.1
33– 4	39.5	576	1.12	2.51	3.60	980	2.0	10.4	6.3	0.03	36	0.94	0.66	1.39	0.17	0.03	<0.01	<0.01	<0.1
33– 5	43.0	676	1.32	2.81	2.15	510	1.0	6.4	2.7	0.03	15.2	0.32	0.34	0.72	0.08	0.02	<0.01	<0.01	<0.1
33– 6	46.8	786	1.54	2.89	1.82	420	0.8	5.4	8.0	0.02	11.3	0.23	0.30	0.60	0.06	0.01	<0.01	<0.01	<0.1
33– 7	63.5	1001	1.96	3.04	1.32	300	0.59	4.2	2.6	0.01	6.2	0.13	0.25	0.41	0.04	0.01	<0.004	<0.01	<0.1
33– 8	67.5	1114	2.18	3.19	1.02														
33– 9	70.5	1221	2.38	3.29	0.840														
33– 10	88.1	1761	3.49	3.45	0.510														
33– 11	91.8	1873	3.66	3.47	0.350	53	0.10	1.12	0.30	0.01	0.4	0.03	0.09	0.08	0.01	<0.01	<0.004	<0.01	<0.1
33– 12	–	1976	3.86	3.50	0.295														
33– 13	117.0	2651	5.18	3.80	0.200	30	0.08	0.74	0.26	<0.01	0.2	0.02	0.05	0.03	0.01	<0.01	<0.004	<0.01	<0.1
33– 14	160.7	3991	7.80	3.93	0.124														
33– 15	164.7	4111	8.03	4.03	0.100	13	0.02	0.37	0.08	<0.01	<0.1	0.01	0.04	0.01	<0.01	<0.01	<0.004	<0.01	<0.1
33– 16	519.5	4695	9.17	2.36	4.60	970	2.06	20.5	17.1	0.04	50.4	1.70	0.58	1.27	0.02	0.04	0.01	<0.01	<0.1
33– 17	522.0	4770	9.32	2.44	3.65	690	1.50	14.7	6.1	0.02	35.5	1.10	0.34	0.92	0.03	0.03	0.02	<0.01	<0.1
33– 18	523.0	4849	9.47	2.50	3.23	[illegible]	1.25	12.5	5.2	0.02	28.2	0.83	0.26	0.75	0.01	0.02	0.01	<0.01	<0.1
33– 19	525.5	4972	9.71	2.57	2.67	440	0.95	9.7	3.9	0.02	19.9	0.57	0.19	0.56	0.01	0.02	0.01	<0.01	<0.1
33– 20	527.5	5064	9.89	2.73	1.93	340	0.71	7.3	5.6	0.01	13.8	0.39	0.17	0.43	0.01	0.01	<0.01	<0.01	<0.1
33– 21	543.5	5629	11.0	2.97	1.09														
33– 22	545.5	5715	11.2	3.18	0.650														
33– 23	550.0	5833	11.4	3.23	0.550														
33– 24	551.5	5960	11.6	3.29	0.450	49	0.10	1.35	0.35	0.01	0.8	0.02	0.05	0.05	0.01	<0.01	<0.004	<0.01	<0.1
33– 25	567.5	6550	12.8	3.43	0.345														
33– 26	570.0	6634	13.0	3.54	0.237														
33– 27	573.0	6749	13.2	3.59	0.210	19	0.02	0.60	0.12	<0.01	0.1	0.01	0.03	0.01	<0.01	<0.01	<0.004	<0.01	<0.1
33	575.5	6861	13.4	3.62	0.195	17	0.02	0.56	0.11	<0.01	0.1	<0.01	0.03	0.02	<0.01	<0.01	<0.004	<0.01	<0.1

APPENDIX F

PROCEDURES AND RESULTS FOR COMPARATIVE LEACHING EXPERIMENTS

I. RCRA LEACHING EXPERIMENTS

The procedure published in the Federal Register of May 19, 1980 [Federal Register 45 (98), 33127] was followed with modifications: (1) we used predried samples because fresh (wet) material was unavailable; (2) we modified the filtration procedure as described below; and (3) we allowed the pH of the Plant D sample to become a little lower than the specified value during the initial addition of acetic acid.

Short-term pretests were made on all samples by adding 400 mℓ deionized water to 25 g solid, thereby determining initial pH values. For those samples with a pretest pH value less than 5 and a history, according to prior Los Alamos leaching procedures, of producing highly acidic leachates, no recording pH meter was used during the 24-h test period, thus allowing simultaneous leaching of several samples. Refuse from Plants B, C, G, K, and I met those criteria. Accordingly, 100 g of −3/8-in. (9-mm) material was put into a 1/2-gal. (2-ℓ) polyethylene bottle, 1600 mℓ deionized (Milli-Q) water was added, the bottle was capped, and the sample was swirled by hand to assure thorough wetting of the solid. The initial pH was recorded. The bottle was placed on its side on a platform shaker and agitation was begun at 90 3-in. strokes per min. Because prior analysis had shown Plant A waste to have some self-neutralizing capacity in the form of calcite and Plant D waste had an initial pretest pH value over 5, those wastes were leached separately, and the test was monitored with a recording pH meter. No automatic titrator was used. The pH electrode was fitted through a rubber stopper that was covered with plastic wrap to prevent contamination from the rubber. Thus, the system was essentially sealed, as were the samples not monitored with the recording pH meter. The pH of the Plant A refuse leachate remained below 5 for the test period, and no addition of acid was necessary. For Plant D waste, the pH was adjusted manually with 0.5*N* acetic acid. An initial 10-mℓ increment of acid lowered the pH from 9.6 to 4.1. Acid was added at 2.5 h, 3.75 h, 18.5 h, and 20 h after agitation was begun to maintain the pH below 5.2. A peak value of 5.75 was reached overnight. A total of 35 mℓ acetic acid was added.

After the samples were removed from the shaker, final pH values were recorded for those samples not monitored continuously. Vacuum filtration was begun according to the Federal Register procedure on Plants B and C samples and the remaining unfiltered samples were refrigerated. After 4 h, filtering was only partially complete. The vacuum was shut off overnight. After 19 h (5 h with vacuum turned on), filtering was still incomplete, though several changes of prefilters and final 0.45-µm filters had been made. At that time, a prefiltering step using a Buchner funnel with Whatman 541 paper was added. Remaining samples were filtered without incident, using the Buchner prefilter step. We rinsed the bottles with 400 mℓ water and added that water to the filter, except for Plant D, to which 365 mℓ was added, making the final volume of liquid 2000 mℓ in all cases. Aliquots of each sample were poured into polyethylene bottles for analysis and all samples were stored in the refrigerator before analysis. (No acid was added for preservation).

Table F-I summarizes the methods used to analyze the leachates. The resultant analytical data are shown in

TABLE F-I

ANALYTICAL METHODS USED FOR RCRA LEACHING EXPERIMENTS

Element	Method	1979 Methods Manual EPA Equiv. Method
As	AA, Hydride[a]	206.3
Ba	AA, N_2O flame[b]	208.1
Cd	AA, Flame	213.1
Cr	AA, Flame[c]	218.1
Pb	AA, Flame	239.1
Hg	AA, cold vapor[d]	245.1
Se	AA, Hydride[a]	270.3
Ag	AA, Flame	272.1

[a] Borohydride reduction.
[b] 1000 ppm Na instead of K.
[c] Air/C_2H_2 flame.
[d] Persulfate oxidation not used.

Table F-II. In Table F-II, $\bar{X}$ is the mean of n independent measurements for the sample and "t" represents the student's t for $\alpha = 0.05$, based on pooled standard deviations for the sample set. The calculations of the β errors are described in Sec. III of the main body of this report. The β error (DWS) represents the probability, based on the analytical data, that the true concentration of the element equals or exceeds the Interim Drinking Water Standard. The β error (RCRA) represents the same probability relative to 100 times the Interim Drinking Water Standards.

II. LOS ALAMOS LEACHING EXPERIMENTS

A. Static (Shaker) Leaches

Representative samples were obtained by splitting from barrels of predried refuse. All samples leached were no greater than 3/8 in. (9 mm) in particle size. In some cases, the samples were pulverized by alumina shell plates to −20 mesh. Previously split samples were tumbled to mix; portions were weighed into flasks and deionized water was added. The sample size was 50 g. The amount of water added was 200 mℓ for Plants A, B, C, and G (4:1 liquid:solid) and 250 mℓ for Plants K and I (5:1 liquid:solid). The container used was a 500-mℓ Erlenmeyer flask with a ground-glass neck, fitted with a glass chimney to allow air access without allowing liquid to splash out during agitation (Fig. F-1). The refuse/water mixtures were placed on a platform shaker and agitated at 90 3-in. strokes per minute. All leaching referred to in this report was done at room temperature (~22°C). After various leaching times, samples were removed from the shaker and filtered by vacuum filtration, using Whatman 541 paper for the first step, followed by either gravity filtration through a fine filter paper (Whatman 42), as with Plants A, B, C, and G samples, or through a Millipore 0.45-μm filter (vacuum filtration), as with samples from Plants K and I. Leachates were diluted by addition of 10% 6*N* HNO_3 for preservation of the sample before analysis.

B. Dynamic (Column) Leaches

Coal or refuse material (0.5 kg) crushed to −3/8 in. was packed into a Pyrex column 70 cm long by 4.6 cm diam in a vertical position. The leaching column was equipped with a necked-down inlet at the bottom for introducing the leachates. A side arm located 5 cm below the open top served as an effluent outlet. Both the upper and lower ends of the coal or refuse bed were retained in the column with loosely packed glass-wool plugs. An upward or countercurrent leachate flow was used in most of the experiments to prevent flow blockage from fine sediment that might settle to the bottom of the column.

The leachate, usually deionized water, was fed through the packed column in one of two ways. Early experiments (Plants A, B, C) used a gravity feed from a reservoir elevated above the column inlet. The flow was regulated by a valve located between the reservoir and the column inlet. Later experiments used a peristaltic pump to feed the effluent through the column. Flow rates used were typically between 0.5 and 1.0 mℓ/min. Measurements of leachate flow and pH were made at the column outlet. Periodically, samples of leachate were collected for analysis of total solids and trace element composition.

C. Analytical Methods

Cadmium, lead, and chromium were determined in the acidified leachates by atomic absorption spectrophotometry. An air acetylene flame was used for chromium. Arsenic was determined by neutron activation analysis.

TABLE F-II

ANALYTICAL RESULTS OF LEACHING TESTS CARRIED OUT ON SEVEN COAL WASTE SAMPLES ACCORDING TO THE EPA EXTRACTION PROCEDURE

	Arsenic (ppm)				Barium (ppm)				Selenium (ppm)				Silver (ppm)			
			Beta Error				Beta Error				Beta Error				Beta Error	
Sample	X ± ts/√n	n	DWS	RCRA	X ± ts/√n	n	DWS	RCRA	X ± ts/√n	n	DWS	RCRA	X ± ts/√n	n	DWS	RCRA
H_2O, Control	<0.001	3	<0.01	<0.01	<0.06	4	<0.01	<0.01	0.0014 ± 0.0006	3	<0.01	<0.01	<0.006	3	<0.01	<0.01
Plant A	0.024 ± 0.001	3	<0.01	<0.01	<0.06	4	<0.01	<0.01	0.0015 ± 0.0006	3	<0.01	<0.01	<0.006	3	<0.01	<0.01
Plant B	0.100 ± 0.004	3	>0.99	<0.01	0.14 ± 0.06	4	<0.01	<0.01	0.0035 ± 0.0007	3	<0.01	<0.01	<0.006	3	<0.01	<0.01
Plant C	0.007 ± 0.001	3	<0.01	<0.01	0.08 ± 0.06	4	<0.01	<0.01	0.0011 ± 0.0006	3	<0.01	<0.01	<0.006	3	<0.01	<0.01
Plant D	<0.001	3	<0.01	<0.01		8	<0.99	<0.01	0.0016 ± 0.0006	3	<0.01	<0.01	<0.00	3	<0.01	<0.01
Plant G	<0.001	3	<0.01	<0.01	0.08 ± 0.06	4	<0.01	<0.01	0.0020 ± 0.0006	3	<0.01	<0.01	<0.006	3	<0.01	<0.01
Plant I	0.016 ± 0.001	3	<0.01	<0.01	<0.06	4	<0.01	<0.01	0.0017 ± 0.0006	3	<0.01	<0.01	<0.006	3	<0.01	<0.01
									0.0038 ± 0.0007	3	<0.01	<0.01	<0.006	3	<0.01	<0.01
HOAc, Control	<0.001	3	<0.01	<0.01	0.08 ± 0.06	4	<0.01	<0.01	0.0009 ± 0.0006	3	<0.01	<0.01	<0.006	3	<0.01	<0.01

	Cadmium (ppm)				Chromium (ppm)				Lead (ppm)				Mercury (ppm)			
			Beta Error				Beta Error				Beta Error				Beta Error	
	X ± ts/√n	n	DWS	RCRA	X ± ts/√n	n	DWS	RCRA	X ± ts/√n	n	DWS	RCRA	X ± ts/√n	n	DWS	RCRA
H_2O, Control	<0.003	3	<0.50	<0.01	<0.005	3	<0.01	<0.01	<0.012	5	<0.40	<0.01	<0.001	4	<0.4	<0.01
Plant A	<0.003	3	<0.50	<0.01	<0.005	4	<0.01	<0.01	<0.012	5	<0.40	<0.01	<0.001	3	<0.5	<0.01
Plant B	<0.004	3	<0.80	<0.01	0.023 ± 0.006	3	0.02	<0.01	<0.012	5	<0.40	<0.01	<0.001	3	<0.5	<0.01
Plant C	<0.003	3	<0.50	<0.01	0.010 ± 0.005	3	<0.01	<0.01	<0.012	5	<0.40	<0.01	<0.001	3	<0.5	<0.01
Plant D	<0.003	3	<0.50	<0.01	<0.005	5	<0.01	<0.01	<0.012	5	<0.40	<0.01	<0.001	3	<0.5	<0.01
Plant G	<0.003	3	<0.50	<0.01	<0.005	5	<0.01	<0.01	<0.012	5	<0.40	<0.01	<0.001	3	<0.5	<0.01
Plant I	<0.003	3	<0.50	<0.01	0.017 ± 0.006	3	<0.01	<0.01	<0.012	5	<0.40	<0.01	<0.001	2	<0.7	<0.01
Plant K	<0.003	3	<0.50	<0.01	<0.005	3	<0.01	<0.01	<0.012	5	<0.40	<0.01	<0.001	3	<0.5	<0.01
HOAc, Control	<0.003	3	<0.50	<0.01	<0.005	4	<0.01	<0.01	<0.012	5	<0.40	<0.01	<0.001	2	<0.7	<0.01

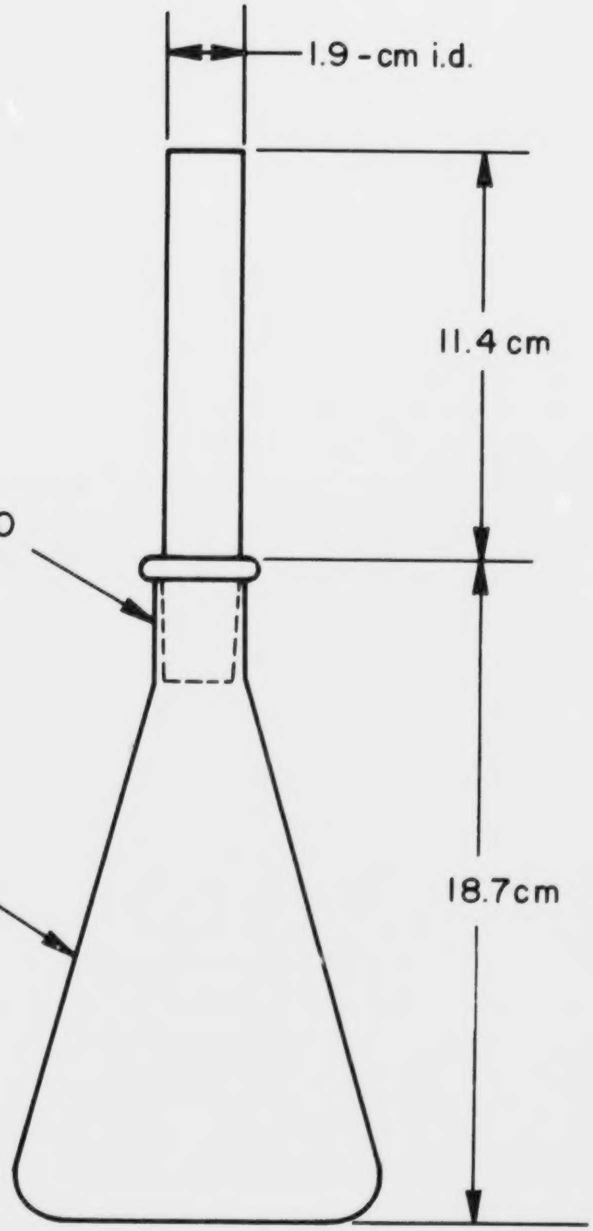
1.9 - cm i.d.
11.4 cm
$ 24/40
JOINT
ERLENMEYER
FLASK, 500 ml.
18.7 cm

Fig. F-1.
Extraction vessel used for Los Alamos shaker leaching experiment.

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16. ABSTRACT The report summarizes work during the 5th year of a trace element characterization of coal wastes. Basically, research was continued on environmental control technologies relating to coal preparation wastes; assessment efforts were extended to include high-sulfur Appalachian coal cleaning wastes. The most promising technology for controlling high-sulfur coal wastes is sequential slurry coating of the waste with lime and limestone. As tested (0.35% lime/1.1% limestone), this technique controlled waste effluent quality for 4 months; effluent pH remained at 7.3-7.6 and trace element concentrations (Al, Ca, Mn, Fe, Co, Ni, Cu) were within acceptable limits according to the EPA MEG/MATE evaluation system. Codisposal of coal wastes with alkaline soils or mine overburdens is partially effective in controlling leachate quality under steady state conditions. However, none of the materials tested could control the highly acidic effluents during intermittent leaching. Comparisons between trace element concentrations predicted by chemical equilibrium models and those observed in coal waste leachates yielded good agreement for the major cations (Al, Ca, Fe); but, except for F, the major anions were not well accounted for. Observed trace element concentrations were all significantly lower than predicted.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Pollution Control	13B
Coal Preparation	Stationary Sources	08I
Wastes	Trace Elements	14G
Waste Treatment	Characterization	
Chemical Analysis	Coal Cleaning	07D
Leaching		07A

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